A TEXT BOOK
OF
HEAT

J. B. RAJAM

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FOR
DEGREE STUDENTS

BY

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Author of

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PREFACE TO THE FOURTH EDITION

The fact that a very large number of copies of the previous edition has been exhausted in a little over one year is proof enough of the usefulness and popularity of the book. In preparing this edition, no major changes from the previous one have been found necessary. A few minor additions, correction of some slips and thorough revision of the text have been made.

My thanks are once again due to the Publishers, Messrs. S. Chand & Co., Ram Nagar, New Delhi. Rajendra Printers, New Delhi, who undertook the printing of the book, are to be congratulated for bringing it out in a neat and presentable form.

December, 1963 J. B. RAJAM

PREFACE TO THE FIRST EDITION

In the preparation of this book, meant for degree students, not only the standard syllabus of the B. Sc. course has been followed, but also the syllabuses proposed by several Indian Universities for the new "three years degree course" have been consulted. The subject-matter, both as regards the arrangement of chapters as well as the contents of each chapter, has been so graded, proceeding from simple to more difficult topics, that the students may follow the course with ease and interest. With this same end in view, the matter dealt with is illustrated, wherever required, by neat and clear diagrams. At the end of each chapter standard questions, taken mostly from the B. Sc. examination papers of our Universities, have been included. Further, to rouse the enthusiasm of the reader, a number of photos of eminent scientists, who have contributed much to the advance of this branch of Physics, has been introduced.

Messrs. S. Chand & Co., Booksellers and Publishers, Delhi, deserve high praise for undertaking the publication of the book in a very commendable and elegant form. The science students, who will use the book, owe a debt of gratitude to these Publishers for the service rendered, to which I add my own sincere thanks, for having suggested to me the idea of writing the book.

September, 1958 J. B. RAJAM

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GENERAL INTRODUCTION

The study of the nature and effects of heat may be said, in a general sense, to have started with the appearance of man on earth. The early man must have felt the heat of the sun during the day and the cold of the night and must have soon learnt to protect himself against very hot summer and intensely cold winter. When it was found that cooked food was more palatable and conducive to health than raw, he must have learnt to produce heat artificially by fire struck between pieces of stick or stone rubbed vigorously. Using leaves and twigs from trees to keep up the fire thus started and vessels, made of earth or metal, to cook his food, even the primitive man must have readily observed that heat was transmitted in material bodies from the hot to the cold side, though not to the same degree in different substances, heat flowing much more quickly in metals than in earthenwares or wood. Heating water in a vessel closed with a loose lid, he must have, now and then, noticed that, when the water began to boil producing copious steam, the lid was violently thrown off. Sometimes, caught in huge forest conflagrations started by accident, he must have realised that fire, though a very useful agent, might easily become a terrible enemy causing devastation and destruction. Following the cycle of seasonal changes, he must have also noted that plants started new life with the appearance of spring's warmth, grew and bore fruit during the hot summer with the accompanying showers of rain, and rested in the cold winter; likewise that ordinary water congealed into *solid* ice during deep winter, melted again into *liquid* water and even slowly disappeared into *gaseous* vapour in the warm season.

Thus, fairly early in man's history, most of the important phenomena connected with heat, as radiation, conduction, different thermal capacities of substances, production of heat by mechanical friction, the converse process of making heat do mechanical work, the continuity of matter in its changes of state under the influence of heat, etc., were observed. But struck by the great usefulness of fire on the one hand and its terrible power of harming on the other, man's first impulse naturally inclined him to deal with it as an object of worship. When this initial awe and respect slowly wore off, as he became adept in controlling fire to serve his needs, and chiefly when he became more scientific minded, he began to test and study in detail his first observations ; useful data were thus slowly gathered in the course of centuries, which now constitute that interesting branch of Physics called Heat.

The aim of a course on Heat is to deal with the various discoveries made concerning the nature and effect of heat in a systematic and scientific manner. This implies that without being satisfied with a mere accumulation of experimental data, these data should be next properly classified by adequate mathematical relations and explained by cogent theories, wherever possible. We shall try to adopt this method of procedure, so that the knowledge we acquire of the phenomena of Heat may be considered really scientific.

CHAPTER I

THERMOMETRY

Introduction. Ordinary we use the sense of touch to find whether a body is hot or cold. A hot body is said to be at a higher temperature than a cold one. Hence *temperature* defines the thermal state of a body, *i.e.*, the degree of hotness or coldness of the body. The method of determining the temperature of a body by the sense of touch is evidently qualitative and often defective, depending very much on the subjective state of the observer. In scientific work involving precision we need a more accurate and objective means and this is known as *thermometry*.

Thermometry may be defined as the art or device of measuring temperature with scientific precision. The *basic principle* of thermometry is that two bodies in contact and in thermal equilibrium have the same temperature. In *practice*, thermometry involves. :

(*a*) *the construction of an instrument*, known as a *thermometer*, based on certain physical properties of matter, such as expansion, electrical resistance, etc., which are readily affected by the thermal state of matter, in a fairly regular manner ; the choice of the *thermometric substance*, which defines both the matter and its state chosen, *i.e.*, solid, liquid or gas, and the physical property used, *i.e.*, expansion, electrical resistance, etc., is determined by the range of temperature to be measured as well as the accuracy of result desired ;

(*b*) *the calibration of the instrument*, which consists in (*i*) fixing certain points on it, easily reproducible in a constant fashion under the same conditions of temperature, known as the *fixed points—e.g.*, the *ice-point*, corresponding to the temperature of melting of pure ice and the *steam-point* giving the temperature of boiling of pure water, and (*ii*) conveniently dividing the interval between the points thus chosen into equal parts,. to which are assigned arbitrary numerical values of temperature, known as the *thermometric scale e.g.*, the Centigrade, Fahrenheit, etc.

(*c*) *the sensitiveness of the instrument*. A thermometer is considered sensitive if it (*i*) quickly takes up the temperature of the body with which it is put in contact and (*ii*) detects even small changes of temperature.

Different kinds of thermometers are in use, which may be broadly classified as follows :—

Liquid thermometers based on the thermal expansion of liquids, such as mercury, alcohol, etc.

Gas thermometers working on the thermal expansion of gases

Resistance thermometers depending on the variation of electrical resistance of metals with temperature.

Thermoelectric thermometers based on the production of e.m.f. due to the difference of temperature of the junctions of two dissimilar metals.

Vapour pressure thermometers which depend for their action on the variation of vapour pressure with temperature.

Radiation thermometers which determine the temperature of a body by measuring the thermal radiation emitted by it.

Here we shall deal with the first four only, postponing the two last ones to later chapters on Low Temperature Technique and Radiation respectively. It may be already noted, however, that in general the use of any particular kind of thermometer depends very much on the range of temperature to be measured and the accuracy of result desired. Thus, for instance, while the mercury thermometer is a simple, convenient device for measuring ordinary temperatures with a sufficient degree of accuracy, a well constructed gas thermometer can measure much wider ranges of temperature with a much greater sensitivity ; the resistance and thermoelectric thermometers can be used to measure fairly high and low temperatures, whereas radiation thermometers are best suited for inaccessible sources and for much higher temperatures than those covered by the others. More details concerning this point, and the relative merits of the different kinds of thermometry, will be mentioned in their appropriate places.

LIQUID THERMOMETERS

1. Mercury thermometer. Of the liquid thermometers, the one commonly used in scientific work for ordinary temperature measurements is the mercury thermometer. It consists of a cylindrical glass bulb containing mercury to which a graduated capillary tube of uniform bore is attached.

Mercury as the thermometric fluid. Fahrenheit was the first to choose mercury as the thermometric fluid on account of its many advantages :—It can be easily obtained pure and remains a liquid over a fairly wide range of temperature ; its expansion is nearly uniform and regular at ordinary temperatures and, being practically non-volatile, is affected very little by its vapour pressure ; it has a low specific heat, so that it does not remove much of the heat of the body whose temperature is measured ; on account of its high conductivity, it quickly assumes the temperature of the body with which it is in contact ; being an opaque and shining liquid, it can be easily seen through glass. But it is to be stated that mercury has the following drawbacks :—Its high specific gravity, setting a limit to the size of the bulb of the thermometer, lowers the sensitiveness of the instrument. Since it has a large surface tension and does not wet glass, its motion in the capillary stem is bound to be somewhat jerky ; also the angle of contact with glass when mercury is rising is different from that when it is falling and this will naturally vitiate correct reading of temperature. The apparent expansion of mercury in glass for a given range of temperature being comparatively very small, the mercury thermometer cannot be very sensitive. As mercury freezes at – 38·8°C and boils at 356°C, the mercury thermometer is pretty much limited in range and cannot be used for very low or very high temperature measurements.

Alcohol as the thermometric fluid. On account of some of these defects, *alcohol* is sometimes used instead of mercury. *The advantages of alcohol over mercury* as the thermometric substance are :—Alcohol, remaining a liquid up to –112°C, is better suited for low temperature measurments. On account of the much larger expansion of alcohol, an alcohol thermometer will be much more sensitive than the mercury thermometer, the other conditions, such as the size of the bulb and stem, being the same ; also errors caused by the expansion of the bulb will be greatly minimised. Alcohol being far less dense than mercury, large bulbs can be used with it, which increases considerably the sensitiveness of the thermometer. Since alcohol has a very low surface tension and wets glass, its motion in the stem will be regular. But there are also the following disadvantages in using alcohol :—Since it is difficult to obtain air-free alcohol, small bubbles of air appear in the bulb or stem of the themometer. As alcohol boils at a rather low temperature (78°C), the upper limit of temperature that can be measured with an alcohol thermometer is low, about 60°C. There is also the probability of alcohol distilling over to the colder parts of the exposed stem of the thermometer, while the bulb itself is in a warm bath. The alcohol thermometer is not suited to measure a rapidly falling temperature, due to the possibility of a thin film of alcohol sticking to the walls of the tube and lagging behind the main column.

The **thermometric glass** *i.e.*, the glass used in making the thermometer must possess the following qualities : it should be stable and should quickly return to its normal state after exposure to high temperatures during manufacture. "Verre dur" glass is used for ordinary thermometers, while "Jena 1 (" for better type and borosilicate glass for those meant for high temperature measurement.

Sensitiveness of a mercury thermometer. Mercury, having a high conductivity and a low thermal capacity, satisfies well the first conditon for sensitiveness *viz.*, it can rapidly assume the temperature of the body with which it is in contact, abstracting as little heat as possible. This condition is further enhanced by making the bulb of the thermometer very small with a large surface area, so that the amount of mercury in the bulb is small.

As regards the second condition, since the change of temperature is indicated by the apparent expansion of mercury in glass and the resulting movement of the mercury meniscus in the stem of the thermometer, a mercury thermometer can be sensitive to very small changes of temperature only if there is considerable displacement of the mercury meniscus in the stem. Supposing that V is the volume of the bulb at a given temperature and α the coefficient of apparent expansion of mercury in glass (*i.e.*, apparent increase in volume of mercury for 1°C rise per unit volume) at that temperature, if the bulb and mercury in it be allowed to rise by 1°C, the apparent increase in volume of mercury in the bulb $= V\alpha$. Corresponding to this increase, if the rise in level of the meniscus in the stem of cross-sectional area A is x, then

$$V\alpha = Ax \quad \text{or} \quad x = V\alpha/A.$$

For a given small change of the temperature the thermometer is sensitive if x is large, which is secured if V is made large and A small. Hence by making the volume of the bulb large and the capillary bore of the stem small, the mercury thermometer is made sensitive. Since using a bulb of large capacity goes against the first condition, in the practical construction of sensitive thermometer, one is to be guided by the nature of the work for which the thermometer is intended.

Details of construction of a mercury thermometer. A carefully chosen glass capillary tube of uniform bore and fairly thick wall is taken. A cylindrical bulb of suitable size is blown at one end of the tube. At the other end, a small reservoir and a pear-shaped funnel are likewise constructed. The size of the bulb and the length of the capillary stem are such that at the lowest temperature which the thermometer has to measure, the mercury will fill the entire bulb and a small portion of the stem. The thermometer tubing thus prepared is cleaned with boiling nitric acid to remove all impurities, washed well with distilled water and dried. It is then set in a vertical position with the cylindrical bulb below and the funnel above. Air-free, pure and dry mercury is poured into the funnel. Mercury will not freely descend into the bulb on account of the narrow capillary bore of the stem. But on slightly warming the bulb, some of the air inside is expelled and some mercury will get into the bulb on cooling. Thus by repeated warming and cooling, taking care that cold mercury coming in contact with the hot bulb does not break it, sufficient mercury is drawn into the bulb. The bulb and stem are then heated until the mercury inside boils. The mercury vapour formed at this stage drives out the air which may otherwise stick to the walls of the tube. On allowing the arrangement to cool, the mercury vapour will condense and the whole of the bulb and stem will be filled with mercury. Next heating to a temperature higher than the maximum temperature which the thermometer will be used to record, the tube is sealed at a point just above the reservoir at the top, using a blow-pipe flame. On cooling, the mercury contracts and the mercury column in the stem sinks, leaving a vacuum in the upper portion of the tube.

Since glass after exposure to high temperatures returns to its normal state only after a very long time, of the order of years, the calibration of the thermometer can be done only after a long lapse of time, whose duration depends upon the nature of the glass used. Even so, corrections will have to be applied for the shift of the zero-point caused by the slow and gradual return of the material of the thermometer to its normal state (*cf.* below).

The calibration of the thermometer, *i.e.*, marking of the two fixed points on the stem and dividing the interval between them into a suitable number of equal parts, is done as follows :—

To get the *lower fixed point* (the ice-point), the thermometer is placed vertically in a bath containing a mixture of pure ice and distilled water, so that the bulb and a small portion of the stem are inside the bath. The arrangement is allowed to stand until the mercury meniscus just visible above the ice-bits remains stationary. This position of the meniscus, which gives the ice-point, is carefully marked on the stem. It is quite essential that the ice used be absolutely free from any salt, since otherwise the point obtained will be lower than the correct one.

To mark the *upper fixed point* (the steam-point), an arrangement, known as the *hypsometer* (Fig. 1), is used. It consists essentially of a boiler B, a double walled long and vertical steam chamber C in which the thermometer T is suspended, a water monometer W which indicates the pressure of steam in the thermometer chamber and a Liebig condenser L to prevent the water from being lost by evaporation. Water is boiled in B and the steam produced passes up through the inside of the thermometer chamber and descends down the outer section (as indicated by the arrows) and goes into the condenser through a side connection, where it is condensed again into water, which flows back into the boiler through the tube R. The top portion of the thermometer is made to jut out of the hypsometer. When the mercury level in the stem, as observed by a microscope M, remains steady, a temporary mark is made on the stem at the stationary position of the mercury meniscus. As the boiling point of water depends on the actual pressure under which the experiment is conducted (decreasing by 0·037° for every mm. decrease of pressure) a correction has to be made before the upper fixed point is permanently traced on the stem.

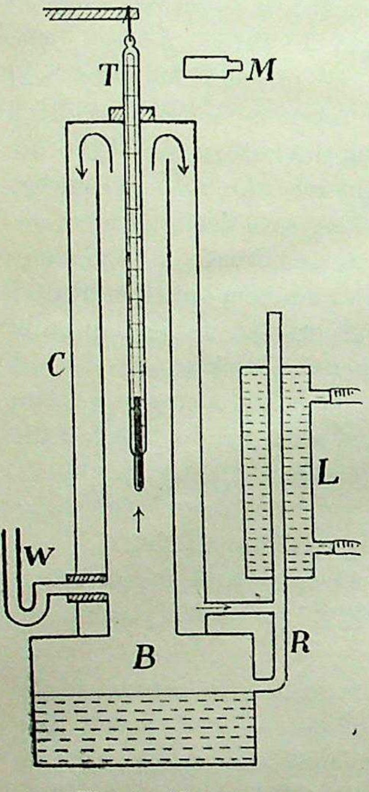


Fig. 1. Hypsometer.

By dividing the length between the two fixed points thus determined into a suitable number of equal parts, the thermometer is provided with a scale to measure temperature conveniently. There are *three different thermometric scales* in use :

(*a*) *The Centigrade scale*, first introduced by Celsius, is generally used in all scientific work. The ice-point is marked 0°C and the steam-point 100°C and the interval is divided into 100 equal parts. Each of these divisions is called one degree centigrade (1°C).

(*b*) *The Fahrenheit scale*, invented by Fahrenheit, is ordinarily used for clinical and meteorological purposes. Here the ice-point is marked 32°F and the steam-point 212°F and the interval is divided into 180 equal parts, each division being called one degree Fahrenheit (1°F). It appears that Fahrenheit chose 32° for the ice-point, because he found with a freezing mixture that the maximum frost temperature was 32° below the temperature of ice.

(*c*) *The Réaumur scale*, first devised by Réaumur, is used for domestic purposes, chiefly in Germany. The interval between the two fixed points is here divided into 80 equal parts, the lower point being marked 0°R and the upper one 80°R, so that each division is one degree Réaumur (1°R).

Since the range of temperature difference between ice and boiling water is the same in all the above three scales, we may write 100 Centigrade degrees = 212 – 32 or 180 Fahrenheit degrees = 80 Réaumur degrees. From this, we have

$$C : F - 32 : R :: 100 : 180 : 80$$

Or

$$\frac{C}{100} = \frac{F - 32}{180} = \frac{R}{80}$$

With this relation, readings on any one scale can be readily converted into corresponding ones on the others.

Errors of a mercury thermometer and their correction. Mercury thermometers, as they can be handled with ease, are generally used for ordinary rough work. If they are employed for precision work, the following errors have to be taken into account and corrected for :—

(*a*) *Secular rise of zero.* Glass, being plastic to a certain extent, when subject to high temperatures during the construction of the thermometer and then allowed to cool, does not return quickly to its original volume. On account of this fact, in a calibrated thermometer the zero-point rises, rapidly at first and then slowly for years. This defect can be greatly removed by properly choosing the material of the glass tubes, annealing the tubes and storing them for years before using them to make thermometers.

(*b*) *Depression of zero.* When a thermometer is exposed to sudden changes of temperature, say from a high to a rather low temperature, the bulb does not at once regain its original volume and there is a consequent depression of zero, whose amount depends both on the kind of glass used and its previous treatment ; the higher the temperature and the longer the duration for which the bulb is exposed, the greater is the depression of zero. It takes days and even weeks for the effect to disappear, if the temperature to which the bulb has been subjected is high. This zero error can be corrected for by a long and tedious method, devised by the Bureau International, known as the "*movable zero method*". It consists in first determining the steam-point (100°C) and immediately after the ice-point (0°C) with the given thermometer. Let its readings at 100°C and 0°C be a and b. Using a bath temperature t°C, let the thermometer reading be a_t. Immediately after this, let the thermometer be placed in an ice-bath and the reading b_t recorded. Then the correct temperature of the bath t°C is given by

$$t = \frac{(a_t - b_t)\,100}{(a - b)}$$

(*c*) *Error in the fixed points* is corrected as follows. For the *lower fixed point,* the thermometer is placed in a suitable ice-bath and the reading of the steady mercury meniscus taken. Supposing it is 0.1°C below the zero mark, the freezing point correction is +0·1°C (additive). If the meniscus reading is above the zero mark, the correction is subtractive. For the *upper fixed point,* the thermometer is checked with a hypsometer, as described previously (*Cf.* p. 8). Suppose the thermometer reads 99·8°C after the steady state is reached under a pressure of 75·8 cms. of mercury. Since the boiling point of water at this pressure is 99·93°C, the correction to be applied is 99·93 − 99·8 = 0·13°C and is positive. If the observed boiling point is above the correct calculated one, the correction is evidently negative.

(*d*) *Correction due to changes in the size of the bulb caused by variable internal and external pressure.* The application of increased pressure to the outside of a thermometer, whether through the rise of barometric pressure or immersion in liquids or compressed gases, reduces the internal volume of bulb. This makes the mercury rise in the stem, for which a correction is necessary. Assuming the increase in pressure to be uniform over the whole external surface of the thermometer, the mercury-rise in the stem will bear a constant ratio to the increase of pressure causing it, which is known as the *external pressure coefficient.* Subjecting the thermometer to known external pressures, the above coefficient can be estimated. Now if the external pressure acting on the thermometer at the time of the actual use of the thermometer to read temperature is known, the correction to be applied can be readily determined.

If a thermometer is used in a vertical position, as is often done, the weight of the vertical column of mercury exerts a pressure, which expands the bulb and thereby causes mercury in the stem to fall. Correction for this can be made by estimating, as in the previous case, the ratio of the fall in the mercury level to the increase in the internal pressure, known as the *internal pressure coefficient*, which is a constant. Or better still, the error can be avoided by using the thermometer in a horizontal position.

(e) *Want of uniformity in the bore of the thermometer tubing.* As capillary tubes are drawn and not bored, slight inequalities in the diameter of the bore are bound to exist in the stem of the thermometer even after very careful selection. This necessitates slight corrections to be applied to the readings observed with the thermometer and it is done as follows. A small portion of the thread of mercury is detached from the rest and its length measured when it occupies different parts of the stem successively, say between 0 and 10, 10 and 20 ... 90 and 100° marks. The measured lengths of the thread will vary from place to place depending upon the diameter of the bore, and let them be $l_1, l_2 \ldots l_{10}$. Let the corrections to be made for want of uniformity of the bore in the vicinity of the 0, 10, 20 ... 100 graduations be $\delta_0, \delta_{10}, \delta_{20} \ldots \delta_{100}$ respectively. If l is the accurate length of the mercury thread used,

then
$$l = l_1 + \delta_{10} - \delta_0 \qquad \ldots (1)$$
$$l = l_2 + \delta_{20} - \delta_{10} \qquad \ldots (2)$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad \ldots$$
$$l = l_{10} + \delta_{100} - \delta_{90} \qquad \ldots (10)$$

Adding up,
$$10\,l = (l_1 + l_2 + \ldots + l_{10}) + (\delta_{100} - \delta_0) \quad \ldots (11)$$

δ_{100} and δ_0 are the corrections of the upper and lower fixed points which can be determined experimentally, as already indicated. Hence l can be estimated from relation (11). Using this value of l, in the various other relations, (1), (2)..., we get

$$\delta_{10} = (l - l_1) + \delta_0$$
$$\delta_{20} = (l - l_2) + \delta_{10}$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

A graph is drawn with the marked scale divisions as abscissae and the corresponding corrections as ordinates. From this graph correction for any intermediate temperature reading is readily obtained.

It is to be noted that the above method is not only tedious but also difficult to carry out in practice. It can be avoided, as is done in some of the standard English thermometers, by the following device used in the calibration itself. The interval between the two fixed points is subdivided not into equal parts but into equal volumes to represent the degrees, so that the volume of the stem between any two degree marks is the same everywhere. Evidently the degree marks will not be equidistant, but closer in parts where the bore is wide and farther apart where the bore is narrow. Here also the capillary tube has to be calibrated for non-uniformity of the bore, but it is done before the tube is transformed into a thermometer.

(*f*) *Error due to capillarity.* The surface tension of mercury causes an excess of pressure inside the meniscus over that outside. This excess of pressure depends on the radius of the capillary tube at the point where the meniscus lies ($p = c/r$, where p is the capillary pressure, r the radius of the tube and c a constant $= 32{\cdot}4$ mgm. per mm.). Since the stem is not uniform in bore everywhere, there will be variations of internal pressure as the thread of mercury rises or falls. These irregular variations of internal pressure make the thermometer less accurate.

The angle of contact between mercury and the sides of the tube varies a good deal as the mercury column rises or falls—the meniscus being flatter when the column is falling than when it is rising. In consequence a rising thread always gives somewhat lower reading than a falling one at the same temperature. But it is also found that the mercury thread is less disturbed by capillarity when it rises than when it falls. Hence it is preferable to take all readings with a rising column.

(*g*) *Emergent column or exposed stem.* In general, when the temperature of a bath is measured, the bulb of the thermometer and a portion of the stem are kept immersed in the bath and the reading is taken. In such cases, a good part of the stem and the mercury contained in it are outside the bath and exposed to the atmosphere, and hence do not acquire the temperature of the bath. On account of this, the thermometer will read less than the true temperature of the bath, the reading being considerably lower if the bath is at a temperature much higher than the room temperature and a greater portion of the stem emerges out of the bath. The correction for this is applied as follows :—

Let the thermometer be immersed in the bath up to the division t_1 on the stem. Let t be the temperature actually read and t' the average temperature of the emergent column, as found with a special integrating thermometer with a long bulb placed near the thermometer to be corrected, with its centre coinciding with the centre of the exposed part. Let v_0 be the volume of one division of the stem at 0°C, m the coefficient of absolute expansion of mercury and g the coefficient of cubical expansion of glass. If x is the required correction, the corrected true temperature will be $(t + x)$°C.

The volume of the emergent mercury is $v_0\,(t - t_1)\,(1 + gt')$ and its temperature is t'°C.

Hence the volume of this mercury at t°C

$$= v_0\,\frac{(t - t_1)\,(1 + gt')\,(1 + mt)}{(1 + mt')}$$

and this would give the correct reading. As the true reading point should be $(t + x)$°C, the volume of mercury at $(t + x)$°C

$$= v_0\,(t + x - t_1)\,(1 + gt)$$

$$\therefore\ v_0\,(t + x - t_1)\,(1 + gt) = v_0\,(t - t_1)\,(1 + gt')\,\frac{1 + mt}{1 + mt'}$$

Solving this equation for x, we get

$$x = \frac{m - g}{(1 + mt')\,(1 + gt)} \times (t - t_1)\,(t - t')$$

Knowing all the quantities on the right hand side x can be estimated.

This correction can be avoided if the bulb and the stem up to the mercury meniscus are put inside the bath, which however is not possible in many cases.

(*h*) *Correction for "lag"*. Another source of error is the fact that thermometers require a sensible amount of time to follow a change of temperature. This is known as the "lag". In a mercury thermometer, the lag increases with the mass of mercury and the thickness of the glass ; it also depends on the nature of the surrounding medium.

If the thermometer is used to measure the constant temperature of a bath, it will in a short while reach the steady temperature of the bath and no correction is necessary. But the most ordinary case in the laboratory is when the temperature of the bath also is rising or falling ; then the thermometer will 'lag' behind the true temperature, indicating a value lower than the true temperature when the bath temperature rises and a higher value when the bath temperature falls.

The phenomenon can be analytically treated as follows :—Let θ be the temperature indicated by the thermometer and θ' that of the bath at any instant. Then the lag $= (\theta' - \theta) = -(\theta - \theta')$, since the lag is generally represented as a negative quantity. Making a legitimate assumption that the lag does not depend on the actual temperature of the bath, but only on the rate at which the temperature is changing, $d\theta/dt \propto -(\theta - \theta')$.

$$\therefore \qquad \frac{d\theta}{dt} = -K(\theta - \theta'),$$

where K is a constant.

Integrating both sides, after separating the variables,

$$\int \frac{d\theta}{(\theta - \theta')} = -\int K dt$$

$$\log(\theta - \theta') = -Kt + \log A$$

$$\therefore \qquad \log\left(\frac{\theta - \theta'}{A}\right) = -Kt$$

$$\text{Or} \qquad \frac{\theta - \theta'}{A} = e^{-Kt}$$

$$\therefore \qquad \theta - \theta' = Ae^{-Kt}$$

Hence the lag varies exponentially with time.

To evaluate A, if θ_0, θ_0' are the temperature indicated by the thermometer and the actual temperature of the bath respectively at $t = 0$,

$$\theta_0 - \theta_0' = A$$
$$(\theta - \theta') = (\theta_0 - \theta_0')\, e^{-Kt}$$

This expression gives the lag of the thermometer at any instant; K can be determined by using a constant temperature bath and measuring the rate of change of the thermometer reading $d\theta/dt$ for a difference of temperature $(\theta' - \theta)$, since

$$K = \frac{d\theta/dt}{(\theta' - \theta)}.$$

In practice, the correction for lag is made as follows : Considering the case when the temperature of the bath is continuously rising, the thermometer readings with time are recorded in a graph with time as abscissa and temperature as ordinate as shown in Fig. 2. The curve PQ represents the thermometer readings with the progress of time. Due to to the lag of the thermometer, the actual temperature of the bath will be somewhat higher at every point on the curve. To make a correction for this, an auxiliary experiment is performed. The bath is maintained at a constant temperature, somewhat higher than the maximum recorded in the main experiment. The thermometer is introduced into the bath and its readings recorded at short intervals of time until the temperature of the bath is reached. If the differences of temperature between the thermometer and the bath are plotted against time, a curve CD is obtained, as shown in Fig. 3. At D, the difference of temperature becomes too small to be observed.

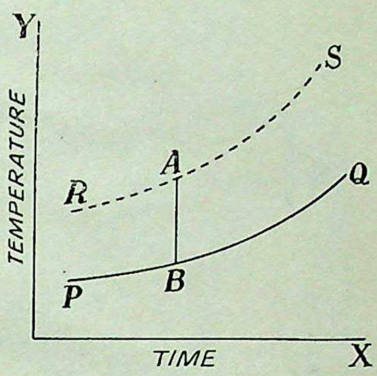


Fig. 2.

Since the slope ($d\theta/dt$) at a point B in the curve PQ (Fig. 2) which gives the rate of change of temperature at that instant is a measure of the amount of lag at the same instant, if a point N is found on CD (Fig. 3) where the slope of the curve is the same as that at B on PQ, the lag at N is the same as that at B. Since NM is the lag at N, if we make BA = NM, then A will give the actual temperature of the bath corrected for lag. Continuing this process for a number of other points on the curve PQ, we get a curve RS above PQ (Fig. 2), representing the corrected temperatures.

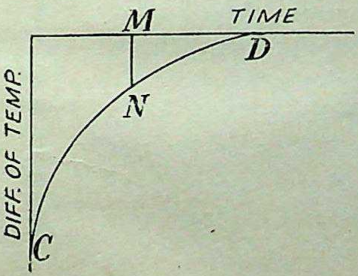


Fig. 3.

2. Beckmann thermometer. Beckmann devised a special form of mercury thermometer to measure very small changes of temperatures of the order of 1/100th of a degree, which is not possible with the ordinary thermometer. It consists of a fairly large bulb with a stem of usual length and bore. The top end of the stem is bent as shown in Fig. 4, with a reservoir R blown in the bent portion. The stem is marked with only 5 or 6 centigrade degrees, but each degree is divided into 100 equal parts. The whole thermometer is enclosed in a glass tube and provided with a brass cap at the top.

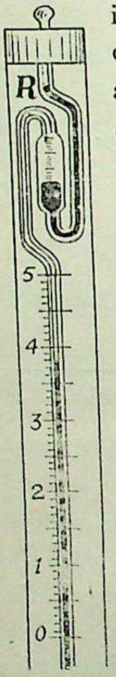


Fig. 4. Beckmann thermometer.

This thermometer can be used to read small variations of temperature to a high degree of accuracy, but only at any given particular small range. The reservoir at the top enables the thermometer to be set at any desired range. The bulb is heated until the mercury thread goes up to the reservoir; the instrument is now gently tapped so that the mercury column breaks near the reservoir and some mercury enters the reservoir. Next the thermometer is placed in a bath whose temperature is varied until the mercury thread stands at the zero division. The temperature of the bath corresponding to the zero of the Beckmann thermometer is noted with an ordinary thermometer. In the vicinity of this temperature, the Beckmann thermometer can record accurately very small changes of temperature. By varying the amount of mercury driven into the reservoir, the thermometer can be adjusted to be near any desired region. With different settings of the zero, the quantity of mercury in the bulb changes and in consequence the value of each scale division also varies. Usually a correction curve for the different settings is supplied with the thermometer, from which the necessary alteration in the value of the scale can be made.

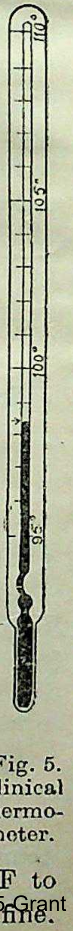


Fig. 5. Clinical thermometer.

3. Clinical thermometer. This type used by doctors is a mercury thermometer of short range which covers a few degrees on either side of the average temperature of the human body — 98·4°F. Usually the range is from 95°F to 110°F. The bulb is very thin and the bore of the stem very fine.

There is a constriction in the stem just above the bulb; mercury passes easily through it when the temperature rises, but cannot do so when the temperature falls. The mercury thread and the scale are made easily visible by making the front part of the thermometer prismatic in shape, which gives a magnified image of the thread and scale when viewed at a proper angle. Usually a small triangular black mark is made on the stem at 98·4°F, the normal temperature.

To find the temperature of the body, the bulb of the thermometer is placed under either the tongue or the arm-pit for good contact for about two or three minutes. As the thermometer picks up the temperature of the body, the mercury expands and passes the constriction without difficulty. Then the thermometer is taken out and the temperature read without hurry, as the mercury column does not fall due to the constriction. To bring back the thermometer to its normal state, it is shaken vigorously so that the mercury passes through the constriction and goes into the bulb.

4. Six's maximum and minimum thermometer. The maximum and minimum temperatures of the atmosphere in a given place during a certain period of time are required for meteorological purposes. Six designed a suitable form of thermometer, shown in Fig. 6, which registers by itself the maximum and minimum temperatures reached during the day of 24 hours. It consists of a cylindrical bulb B connected to a bent tube CD. The whole of B and a part of C contain alcohol. The remaining portion of C and a part of D contain mercury. Above the mercury in D there is alcohol filling up to a part of the bulb R. The rest of the space in this bulb contains alcohol vapour. The tubes C and D are directly calibrated into degrees, either centigrade or Fahrenheit, so that the temperature can be read on the scales. In each arm of the bent tube, over the mercury meniscus, there is a small and light, dumb-bell shaped glass or steel index I, fitted with an iron wire

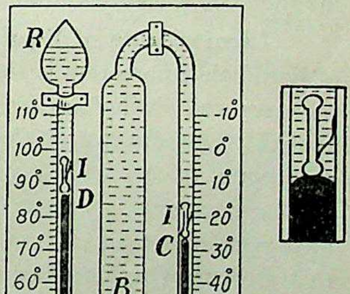


Fig. 6. Six's maximum and minimum thermometer.

which acts as a spring pressing against the wall of the tube (shown separately).

When the temperature of the surrounding air rises, the alcohol in B expands, the mercury in C is pushed down, so that its level in D goes up. Along with it, the index is pushed upwards to a maximum limit, depending on the maximum temperature reached. When the temperature falls, this index remains undisturbed due to the action of the attached spring and the low viscosity of alcohol, while the index in C is pushed upwards by the rising mercury as the alcohol in B contracts. When the temperature, after reaching a minimum value, rises again, the index in C is left behind at the position up to which it has been pushed. The lower end of the index in D gives the maximum temperature, while the lower end of the index in C the minimum temperature. The two temperatures can be read at leisure, even at a time when the actual temperature is neither maximum nor minimum for the period considered. The thermometer is reset for the next record, by bringing the two indices into contact with their respective mercury levels, a small magnet being used from outside for the purpose.

Limitations of liquid thermometers. The chief drawback of liquid thermometers is that, if they use different liquids such as mercury and alcohol and are calibrated as stated above, they will probably agree only at 0°C and 100°C, but at no other temperature, on account of the fact that the expansion of the different liquids is neither regular nor similar. Hence such thermometers give an arbitary scale of temperature. Also, the many corrections to be applied to a mercury thermometer cannot be made rigorously. In practice, therefore, it is usually calibrated by comparsion with the more reliable resistance thermometer ; even then it is hardly suited for precision work since at best it can only read to an accuracy of 0·05°C.

GAS THERMOMETERS

1. Gases possess several advantages as thermometric substance over liquids. They *expand much more than liquids* for the same increase of temperature. Thus, for 1°C rise of temperature, a permanent gas expands twenty times as much as mercury. Hence, gas thermometers will be more sensitive and the expansion of the container will lead to a negligible correction. The *expansion of gases is also quite regular* over a much wider range of temperature than in the case of liquids. A permanent gas, for instance, when not subjected to high pressures, maintains its state and behaves in the same manner at very high as well as very low temperatures, while mercury is limited by its freezing and boiling points. *Gases have much lower thermal capacity* than liquids and in consequence are more sensitive to gain or loss of heat. Gases also possess *very low specific gravity* and can be *obtained of the same purity* in any part of the world ; the only precaution necessary is to have them in a *perfectly dry state*, which can be done with the help of drying agents. *The scale furnished* by different gases *are almost identical*, since the volume and pressure coefficients of all permanent gases are nearly equal. This is the reason why gas thermometers are taken as *primary standards*, and all other thermometers are compared with them for calibration and hence called *secondary thermometers.*

2. **Principle of gas thermometers.** The use of gas as thermometric substance is based on the two well-known *Boyle's* and *Charles' laws*. The former states that the volume of a given mass of a gas varies inversely as its pressure, the temperature remaining constant, or pv = a constant at constant temperature. The latter is usually stated in two forms :—

(*a*) the volume of a given mass of a gas is directly proportional to its absolute temperature, the pressure remaining constant, or v / T = a constant at constant pressure ;

(*b*) the pressure of a given mass of a gas is directly proportional to its absolute temperature, the volume remaining constant, or p / T = a constant at constant volume.

Charles' law follows immediately from the experimental study of the expansion of gases, which clearly points out that the coefficient of volume (or pressure) expansion at constant pressure (or volume) is almost the same for all gases and is equal to $^1/_{273}$ or 0·00367. Representing the two coefficients by α_v and α_p respectively, we have

R. Boyle

$$v = v_0 (1 + \alpha_v t) \qquad \ldots (1)$$

where v_0 is the volume of a given mass of a gas at 0°C and v its volume at t°C, at constant pressure,

$$p = p_0 (1 + \alpha_p t) \qquad \ldots(2)$$

where p_0 is the pressure of a given mass of a gas at 0°C and p its pressure at t°C, at constant volume, and

$$\alpha_v = \alpha_p = {}^1/_{273} \qquad \ldots(3)$$

Taking (1) and substituting the numerical value of α_v, we have

$$v = v_0 \left(1 + \frac{t}{273}\right) = v_0 \left(\frac{273 + t}{273}\right) \qquad \ldots(4)$$

When $t = -273$°C, the quantity inside the bracket becomes zero and $v = 0$. Hence at -273°C, the volume of a gas at constant pressure is zero, so that -273°C represents the lowest possible temperature attainable by a gas.

Similarly, substituting in (2) the value of α_p,

$$p = p_0 \left(\frac{273 + t}{273}\right) \qquad \ldots(5)$$

Again, we see that at -273°C the pressure of a gas at constant volume becomes zero. This temperature (-273°C) is called the *absolute zero* of temperature. If we measure temperature from this zero, the ice-point is given by 273°, the steam-point by $(273 + 100)$° and any temperature t°C by $(273 + t)$°. Such a scale of thermometry is known as the *Kelvin* or *absolute scale* and $(273 + t)$° on that scale is usually written as T°K or T°A.

Equations (4) and (5) can be written on this absolute scale as :

$$v = \frac{v_0 T}{273} \text{ and } p = \frac{p_0 T}{273} \qquad \ldots(6)$$

These relations (6) show that $v \propto T$ and $p \propto T$ since v_0 and p_0 are constant. This is Charles' law.

Note : In defining the absolute zero, the pressure of a gas becoming zero is preferred to its volume becoming zero, since it is inconceivable that matter should at any time occupy no space, while pressure which, according to the kinetic theory of gases, is caused by molecular bombardment, can be conceived to cease to exist at the absolute zero, as we shall see in a later chapter.

Perfect gas equation. The laws of Boyle and Charles are found to be obeyed only approximately by the permanent gases found in nature, but rigorously by a perfect gas. In this latter case, the two laws can be combined into a single one, known as the 'perfect gas equation', as follows :—

Let the gas be initially at pressure p_1, volume v_1 and temperature T_1°K. Supposing first that its pressure changes from p_1 to p_2 while the temperature remains constant at T_1, the resulting volume v is given, according to Boyle's law, by

$$p_1v_1 = p_2v \qquad \text{... (1)}$$

Next, if the temperature changes from T_1 to T_2, the pressure remaining constant at p_2, the final volume v_2 is given, according to Charles' law by

$$\frac{v}{T_1} = \frac{v_2}{T_2} \qquad \text{... (2)}$$

Combining (1) and (2),

$$\frac{p_1v_1}{T_1} = \frac{p_2v_2}{T_2} \qquad \text{... (3)}$$

Relation (3) can be written in a general form as :

$$\frac{pv}{T} = \text{constant} \qquad \text{... (4)}$$

This is the perfect gas equation ; the constant is known as the *gas constant*, which evidently varies as the mass of the gas taken, since Boyle's and Charles' laws imply that the mass of the gas should be kept constant. It is usually referred to 1 gram of a gas and is measured in *ergs per degree centigrade per gram.*

Universal gas constant. Considering one gram-molecule, the above constant is usually denoted by the symbol R and is found to be the same for equivalent gram molecules of all gases, since by Avogadro's hypothesis the gram-molecular volume of all gases is the same under the same conditions of temperature and pressure. R is known as the universal gas constant and the perfect gas equation is written as

$$pv = RT \qquad \text{...(5)}$$

The numerical value of R can be estimated as follows :—

For any gas at N.T.P. the gram-molecular volume is 22·4 litres Substituting numerical value of p, v and T in equation (5)

$$(76 \times 13{\cdot}595 \times 980) \times (22{,}400) = R \times 273$$

$$\therefore \quad R = \frac{76 \times 13{\cdot}595 \times 980 \times 22400}{273}$$

$$= 8{\cdot}313 \times 10^7 \text{ ergs per deg. centigrade per gram-mol.}$$

Since 1 calorie = $4{\cdot}2 \times 10^7$ ergs (mechanical equivalent of heat)

$$R = \frac{8{\cdot}31 \times 10^7}{4{\cdot}2 \times 10^7} \text{ cal. per deg. C. per gram-mol.}$$

$$= 1{\cdot}986 \text{ cal. per deg. C. per gram-mol.}$$

If the mass of the gas is increased n times, the volume at the same temperature and pressure is increased n times, and hence the gas constant will also be increased n times, so that the gas equation can be represented in the most general form by

$$pv = n\text{RT} \qquad \ldots(6)$$

where n is the number of gram-molecules considered.

It may be noted that the universal gas constant is equal to the individual gas constant multiplied by the molecular weight.

The deviations from the 'ideal' equation (5) in the case of 'actual' gases will be discussed in a later chapter.

Equation (5) indicates two ways of measuring temperature with gas thermometers :—

(*i*) Keeping the pressure constant and observing the change in volume—*constant pressure thermometer*.

(*ii*) Keeping the volume constant and noting the change in pressure—*constant volume thermometer*.

Two thermometers filled with a perfect gas, *i.e.*, obeying strictly the gas equation, will agree throughout the scale in thair indications, if the temperature is measured by change of volume under constant pressure by one and by change of pressure under constant volume by the other. The temperature registered by the two thermometers is called the absolute temperature. Thermometers filled with actual gases such as air, hydrogen, nitrogen, etc., approximate very closely in their indication to the above mentioned ideal instruments over a considerable range. Further, since the change of pressure at constant volume of hydrogen at ordinary temperatures is found far more regular than in the case of any other gas, in practice, the constant volume thermometer is preferred to the constant pressure thermometer, with hydrogen as the thermometric substance.

3. Description of some important gas thermometers. Simple devices, such as Joly's constant volume apparatus and Regnault's constant pressure arrangement, used for determining the two coefficients of expansion of gases (*cf.* Chapter II) could be employed for measuring temperature. But they are too simple and have too many limitations to serve directly the purpose of reliable gas thermometers for accurate work. Hence, more elaborate instruments have been designed, which, though based on the same principles as the elementary types, have been able to overcome the chief practical difficulties, so that they can be classed as true gas thermometers. One is due to Callendar, known as the *Callendar's compensated thermometer* —a constant pressure air instrument, and another due to Harker and Chappuis, known as the *International Standard thermometer*—a constant volume hydrogen instrument, which the Bureau International des Poids et Mesures in France has adopted as a practical standard and is accepted as such everywhere today. We shall here describe briefly these two thermometers.

Callendar's compensated air thermometer. A silica bulb A, used as the thermometer bulb, is connected by a capillary tube bent twice at right angles to an exactly similar bulb R provided with a tap which serves as a mercury reservoir. The compensating arrangement is another bulb B, also exactly similar to A, placed close to R and fitted with a capillary tube, which is of the same length and bore as the one connecting A and R, both tubes lying side by side so that they may have the same temperature throughout. The two parts of the apparatus are put in communication with a manometer M containing sulphuric acid, so that the pressure of the air in A can always be kept equal to the pressure of the air in B.

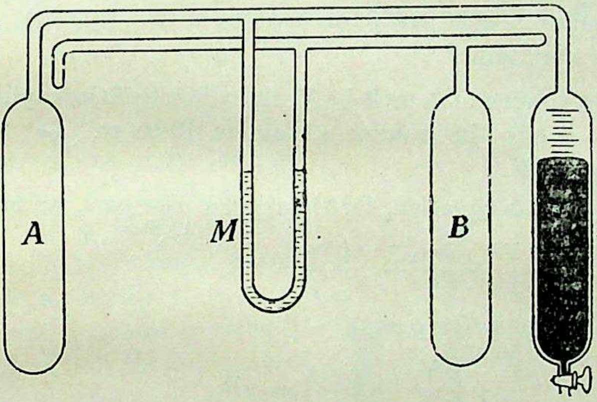


Fig. 7. · Callendar's compensated constant pressure air thermometer.

In the construction of the thermometer all the three bulbs, A, B and R, are immersed in baths of melting ice, with R filled with mercury. The tubes are sealed while in communication with the atmosphere, so that there is *equality of pressure for the air enclosed in A and B* as indicated by the manometer. Henceforth changes of atmospheric pressure will not affect the enclosed air. Since, while equal volumes of air in A and B are at the temperature of ice, the air in the two identical capillary tubes are at the room temperature, *the mass of gas enclosed in the two parts of the apparatus is the same.*

To use the thermometer for measuring temperature, the bulb A is placed in a bath whose temperature T°K is required, while B and R are kept in an ice-bath at T_0°K. When the temperature of the bulb A rises, the air in it expands and passes through the capillary tube into the mercury reservoir. By drawing out mercury through the tap, the equality of pressure in the two parts is restored as indicated by the manometer. The volume of air thus admitted in R is estimated by weighing the mercury drawn out.

Let the mass of air enclosed in each part be n gram-molecules and the pressure in each part p, on account of the equality of mass and pressure maintained.

Let the volume of A or B be V, the volume of the capillary tube in each part v and the volume of air in R be v'. Let the room temperature be t°K.

Using the gas equation, for the *thermometer part*, we have

$$p\left(\frac{V}{T} + \frac{v}{t} + \frac{v'}{T_0}\right) = nR \qquad \ldots (1)$$

and for the *compensating part*

$$p\left(\frac{V}{T_0} + \frac{v}{t}\right) = nR \qquad \ldots (2)$$

Comparing (1) and (2)

$$\frac{V}{T} + \frac{v}{t} + \frac{v'}{T_0} = \frac{V}{T_0} + \frac{v}{t}$$

Or

$$\frac{V}{T} = \frac{V - v'}{T_0}$$

$$\therefore \qquad T = \frac{VT_0}{V - v'} \qquad \ldots (3)$$

If the temperature of the bath is to be measured in the centigrade scale, say as θ°C, putting $T_0 = 273$°K, we get

$$(273 + \theta) = \frac{V \times 273}{V - v'}$$

Or

$$\theta = \frac{v'}{V - v'} \,.\, 273°\mathrm{C} \qquad \ldots (4)$$

This type of thermometer is easily manipulated and found satisfactory for measuring temperatures beyond the range of mercury thermometers. If the compensating part is properly arranged, reliable determination of temperature up to 600°C can be made. The apparatus is fairly simple and the calculations involved in estimating temperatures are quite easy. Callendar has claimed for his thermometer a high degree of accuracy and a good range of utility since results depend only on the accuracy of weighing and internal pressure on the bulb does not vary with temperature. Nevertheless since the instrument has been found not to give consistent results, it has been superseded by the constant volume thermometer, as a practical standard.

Standard constant volume thermometer. It consists of a platinum-iridium bulb A, cylindrical in shape, a metre long, 3·6 cms. in diameter, about a litre in capacity, filled with pure, dry hydrogen at a pressure of 1 metre of mercury at the temperature of melting ice (Fig. 8). It is connected to a special type of mercury manometer by a capillary tube B of platinum, 1 metre in length. The limb C of the manometer contains two columns of mercury separated by a steel piece S, provided with an ivory index or a platinum point P; the other limb D acts also as the cistern of an incorporated barometer, consisting of the bulb F and the long narrow tube E which is bent in such a way that F is in the same vertical line as C, so that the mercury levels in C and F can be conveniently read with a cathetometer and telescope. Both the mercury columns in C, *i.e.*, above and below S, communicate with D. The manometer is provided with an additional mercury reservoir G connected by a long piece of rubber tubing. By raising or lowering G, the ivory index or platinum point is always maintained flush with the mercury level in the lower part of C, so that the volume of the enclosed

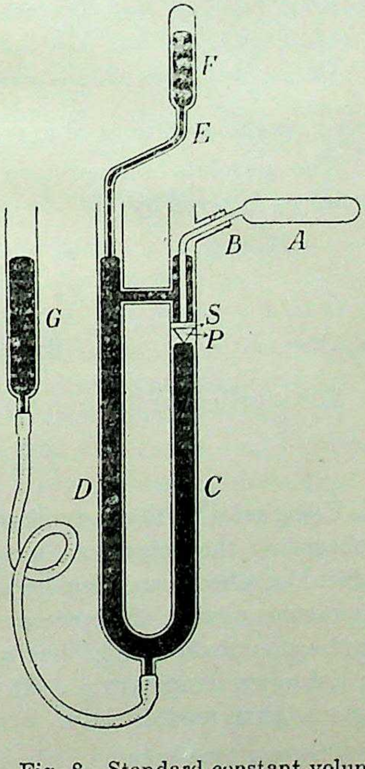


Fig. 8. Standard constant volume hydrogen thermometer.

gas is kept constant. The pressure of the gas at any instant is given by the difference of two readings of the cathetometer, one of the mercury level in F and the other of the index P.

If p_0 and p_{100} denote the pressures of the enclosed gas at 0°C and 100°C respectively, and v its volume maintained constant,

$$p_0 v = n\mathrm{RT}_0 \qquad \dots (1)$$

$$p_{100} v = n\mathrm{R}(\mathrm{T}_0 + 100) \qquad \dots (2)$$

where T_0 represents 0° on the absolute scale.

From (1) and (2)

$$\frac{p_{100}}{p_0} = \frac{\mathrm{T}_0 + 100}{\mathrm{T}_0}$$

Or

$$\frac{1}{\mathrm{T}_0} = \alpha_p = \frac{p_{100} - p_0}{100 p_0} \qquad \dots (3)$$

where α_p is the coefficient of expansion at constant volume.

The absolute temperature T corresponding to any observed pressure p_T is given by

$$\frac{p_\mathrm{T}}{p_0} = \frac{\mathrm{T}}{\mathrm{T}_0}$$

Or

$$\mathrm{T} = \frac{p_\mathrm{T}}{p_0} . \mathrm{T}_0$$

Substituting for T_0 from (3)

$$\mathrm{T} = \frac{p_\mathrm{T}}{p_0} . \frac{100\, p_0}{p_{100} - p_0} = \frac{100\, p_\mathrm{T}}{p_{100} - p_0} \qquad \dots (4)$$

Using relation (4) any unknown temperature can be determined by observing the corresponding pressure with the thermometer. A graphical method can also be employed by plotting some known temperatures against the corresponding pressures as measured by the instrument, and the graph thus obtained being used for measuring other unknown temperatures. It is also possible to calibrate the thermometer to read directly.

The constant volume hydrogen thermometer can be used over a wide range of temperature, from −200°C to 500°C. Above this temperature, hydrogen diffuses through platinum. With glazed porcelain bulb, one can go up to 1100°C. For still higher temperatures up to 1500°C, nitrogen is used ; for low temperatures below −200°C helium is often used.

In accurate measurement, corrections have to be applied for the change in volume of the thermometric bulb due to variations of temperature and internal pressure, for alterations in the density of mercury with temperature, for the gas in the capillary connecting tube and for the dead space between the mercury level and the steel-piece in the manometer. Different gases used in the instrument will give different scales of temperature, if the calibration is made as indicated above. Thus the use of any particular gas will lead to an arbitrary scale of temperature. To avoid this, actual observations must be reduced to that state of the gas where the perfect gas laws are obeyed.

As the gas thermometers are very cumbersome to handle, they are chiefly used for standardising other more convenient devices, such as the resistance thermometer, thermocouple, etc. For the purpose of standardisation, comparison baths, suitable for different ranges are employed, *e.g.*, a water bath for the range 0°C to 100°C, an oil bath between 100°C and 250°C, a mixture of sodium and potassium nitrates from 250°C to 600°C and electric ovens for still higher ranges.

ELECTRICAL RESISTANCE THERMOMETERS

1. Principle. The electrical resistance of a metallic wire is found to increase gradually and fairly uniformly with temperature over a wide range, and consequently on this property a system of thermometry has been devised. The relation between the resistance of a metallic wire and its temperature may be represented roughly by $R_t = R_0(1 + \alpha t)$, where R_0 is the resistance of the wire at 0°C, R_t the resistance at t°C and α the coefficient of increase of resistance, depending on the nature of the wire. If this relation, first suggested by Clausius, were true for all ranges of temperature, the resistance would vanish at absolute zero. Further investigations showed that the above formula did not represent observations accurately even at ordinary temperatures. Callendar was however able to prove that pure platinum wire, free from alloy with silicon, carbon, tin or other impurities, when not subjected to strain or rough usage, possessed always the same resistance at the same temperature and its variation with temperature could be represented by a fairly simple formula of the type $R_t = R_0 (1 + \alpha t + \beta t^2)$ where α and β are constants of the specimen of wire used.

Hence, in the case of pure platinum wire, assuming the simpler relation of Clausius as fairly correct, if R_0, R_{100} and R_t are its resistances at 0°C, 100°C and unknown temperature t°C, we may write

$$R_t = R_0(1 + \alpha t)$$
$$R_{100} = R_0(1 + 100\alpha)$$

$$\therefore \qquad \alpha = \frac{R_{100} - R_0}{100\,R_0}$$

$$t = \frac{R_t - R_0}{R_0\,\alpha}$$

Substituting for α,

$$t = \frac{R_t - R_0}{R_0} \times \frac{100\,R_0}{R_{100} - R_0}$$

$$= \frac{R_t - R_0}{R_{100} - R_0} \times 100 \qquad \ldots (1)$$

The temperature 't' thus determined on the 'platinum scale' is bound to differ from the corresponding temperature 't'' obtained on the standard 'gas scale', since the assumed formula for R_t is not applicable through any extended range. But Callendar found that the difference of the indications of the plantinum resistance thermometer and the standard hydrogen thermometer could be represented over a wide range with great accuracy by the parabolic formula

$$t' - t = \delta \left\{ \left(\frac{t'}{100} \right)^2 - \frac{t'}{100} \right\} \qquad \ldots (2)$$

where δ is a constant for the particular specimen of platinum wire used, and very nearly 1·5 in most cases.

The above relation may be deduced as follows :— Relation (1) may be written as

$$t = \frac{R_t' - R_0}{R_{100} - R_0} \times 100 \qquad \ldots (3)$$

where R_t' is the resistance of the platinum wire at the corresponding temperature t' on the standard 'gas scale'.

Hence $$t' - t = t' - \frac{R_{t'} - R_0}{R_{100} - R_0} \times 100 \qquad \ldots (4)$$

Using the relation $R_{t'} = R_0\,(1 + \alpha t' + \beta t'^2)$

$$R_{t'} - R_0 = R_0\,(\alpha t' + \beta t'^2)$$

Similarly $R_{100} - R_0 = R_0\,\{100\alpha + (100)^2\beta\}$

$$\therefore \qquad \frac{R_{t'} - R_0}{R_{100} - R_0} = \frac{\alpha t' + \beta t'^2}{\{100\alpha + (100)^2\beta\}}$$

Substituting this in (4),

$$t' - t = t' - \frac{\alpha t' + \beta t'^2}{\{100\alpha + (100)^2\beta\}} \times 100$$

$$= t' - \frac{\alpha t' + \beta t'^2}{\alpha + 100\beta}$$

$$= \frac{\alpha t' + 100\beta t' - \alpha t' + \beta t'^2}{\alpha + 100\beta}$$

$$= \frac{100\beta t' - \beta t'^2}{\alpha + 100\beta}$$

$$= \frac{100\beta t'}{\alpha + 100\beta} - \frac{\beta t'^2}{\alpha + 100\beta}$$

$$= \frac{t'}{100} \times \frac{(100)^2\beta}{\alpha + 100\beta} - \frac{t'^2}{(100)^2} \times \frac{(100)^2\beta}{\alpha + 100\beta}$$

$$= -\frac{(100)^2\beta}{\alpha + 100\beta}\left\{\left(\frac{t'}{100}\right)^2 - \frac{t'}{100}\right\}$$

Replacing $-\frac{(100)^2\beta}{\alpha + 100\beta}$ by δ, we get

$$t' - t = \delta\left\{\left(\frac{t'}{100}\right)^2 - \frac{t'}{100}\right\} \qquad \ldots(5)$$

Hence the essential factors involved in the construction of an electrical resistance thermometer are :—(*i*) pure platinum wire, free from alloy or impurities and from strain or chemical alteration, should be used ; (*ii*) the temperature indicated by the platinum resistance thermometer must be compared with the standard gas thermometer and the necessary correction applied.

2. Description of platinum resistance thermometers. Siemens was the first, in 1871, to construct a platinum thermometer based on the principle stated above, but his instrument was not quite satisfactory in constructional details. Improvements made by Callendar and Griffiths have been able to produce the reliable modern type of platinum thermometer, which will be now described.

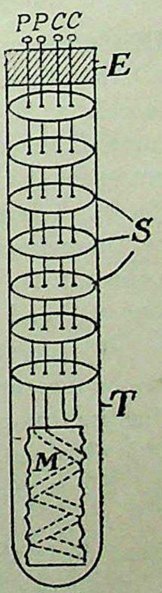


Fig. 9. Platinum thermometer.

Pure, well annealed platinum wire, doubled on itself to avoid induction effects, is wound on a thin flat strip of insulating mica M and placed at the bottom of a hard glass or glazed porcelain tube T, provided with an ebonite cap E (Fig. 9). The free ends of the wire are attached to long leads which pass through holes in several mica sheets S closely fitted along the upper part of T and are connected to binding screws PP fixed in the ebonite cap. For accurate work, up to 700°C, copper leads can be used and the tube can be of glass, but for higher temperatures platinum leads and porcelain tube have to be employed. In order to eliminate the effect due to variation in the resistance of the leads, a pair of *compensating leads*, consisting of a wire of the same material, length and dimension as the leads of the platinum wire, folded into two, pass through holes in the mica sheets close to the other leads and are connected to two binding screws CC in the cap at the top. The tube T is evacuated and sealed to prevent moisture depositing on the mica and rendering the insulation less effective.

3. Callendar and Griffiths bridge. As the determination of temperature with this instrument involves the accurate measurement of the resistance of the platinum wire, Callendar and Griffiths devised a special type of Wheatstone bridge, capable of measuring changes of resistance to a high degree of accuracy, up to ten-thousandth of an ohm. It is shown diagrammatically in Fig. 10. It consists of two ratio arms P and Q of equal resistance. The third arm R is one of adjustable resistance, marked 10, 20, 40, 80, etc. units, each unit being equal to 0·01 ohm. This and the fourth arm S, in which the unknown resistance (platinum wire of the thermometer) is put, are connected to a stretched bridge wire MN of great uniformity whose resistance per cm. is made to be equal to $\frac{1}{2}$ the above mentioned unit. T is a second parallel wire of the same material as MN which may be connected to MN by means of a short length of the same material wire by pressing a button jockey. This arrangement of contact is used to eliminate disturbing thermo-electric effects. T is connected to a galvanometer G. The platinum lead of the thermometer are put in the arm S, while the compensating leads in the arm R. A battery is connected through a tap-key to the junctions of P and R and of Q and S.

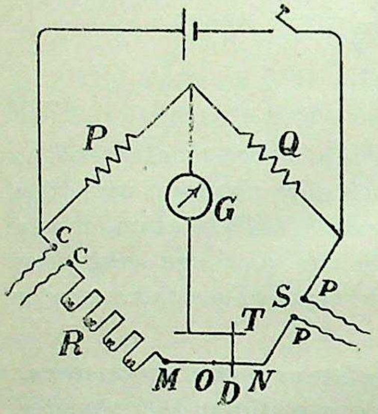


Fig. 10. Callendar and Griffiths bridge.

Placing the platinum thermometer in the bath whose temperature is to be measured, suitable resistance is introduced in the arm R and adjusting the position of the jockey on the wire MN, the balance point 'D' is obtained, as indicated by no deflection in the galvanometer.

Since the ratio arms P and Q are of equal resistance,

$$R + r + \rho \, . \, MD = S + r + \rho \, . \, ND$$

where R is the known resistance introduced in the third arm, r the resistance of either the platinum or compensating leads, which are exactly similar in all respects, ρ the resistance per cm. of the wire MN and S the resistance of the platinum wire of the thermometer at the temperature of the bath to be measured.

$$\therefore \quad S = R + \rho\,(MD - ND)$$

$$= R + \rho\,(OM + OD - ON + OD) = R + 2\rho\,.\,OD$$

O being the mid-point of the wire MN.

Since $\rho = \frac{1}{2}$ unit which is equal to 0·01 ohm.

$$S = R + \cdot 01 \times OD.$$

If the balance point D is to the right of O (as in Fig.) $0{\cdot}01 \times OD$ must be added to R ; if to the left of O, subtracted. Thus the resistance S of the platinum wire of the thermometer at the temperature of the bath is determined accurately. If R_0 and R_{100} are measured in a similar manner, the unknown temperature of the bath can be readily calculated using relation (1), *i.e.*,

$$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100.$$

The quantity $(R_{100} - R_0)$, called the *fundamental interval* of the thermometer, is generally 1 ohm.

The accuracy of the instrument may be estimated as follows :—

Since $\rho = \cdot 005$ ohm, in terms of the fundamental interval (1 ohm), it is equal to $(R_{100} - R_0)/200$. Making R equal R_0, let the balance point be 1 cm. to the right of O.

$$\text{Then} \qquad S = R_0 + 2 \times \frac{R_{100} - R_0}{200}$$

$$\text{Or} \qquad \frac{S - R_0}{R_{100} - R_0} = \frac{1}{100}$$

$$\therefore \qquad 1 = \frac{S - R_0}{R_{100} - R_0} \times 100$$

which shows that the temperature of the bath on the platinum scale is 1°C. Hence, if the balance point is determined correct to 0·1 mm., the temperature can be measured correct to 0·01°C.

To obtain the true temperature from the platinum temperature relation (5), *i.e.*,

$$t' - t = \delta \left\{ \left(\frac{t'}{100} \right)^2 - \left(\frac{t'}{100} \right) \right\}$$

is used ; the constant δ is determined by simply finding the boiling point of sulphur, whose true temperature is known, with the platinum resistance thermometer. For accurate work, the expression on the right hand side of relation (5) is calculated for different assumed values of t' and a table is made giving the value of the correction term $(t' - t)$ for different values of t. With the help of this table the true temperature t' corresponding to any experimentally determined platinum temperature t can be readily found. It was shown by Heycock and Neville that if a platinum thermometer is standardised at 0°C, 100°C and the boiling point of sulphur (444·6°C), the parabolic relation (2) gives correct readings up to 630°C. In practice, however, each platinum thermometer is provided with a temperature-resistance calibration curve drawn from actual comparison with a standard gas thermometer, from which any unknown temperature can be directly read when the corresponding resistance is measured.

4. The advantages of the platinum resistance thermometer are :—(*i*) It is convenient to use ; (*ii*) it has a wide range, —200°C to 1200°C ; (*iii*) if carefully prepared and used, it can read correct to 0·01°C up to 500°C and to 0·1°C up to 1200°C, although it is not advisable to use it above 1000°C an account of the danger of contamination by the insulating materials ; (*iv*) it is as accurate as the gas thermometer and when once standardised it can be used as a reliable standard.

Its *chief drawback* is that, due to the large thermal capacity and low thermal conductivity of the container tube, it cannot quickly attain the temperature of the both in which it is immersed ; also it takes some time to balance the bridge ; hence it is not adapted to measuring rapidly varying temperatures.

THERMOELECTRIC THERMOMETERS

1. Principle. When a circuit is formed of two wires of different metals, say copper and iron, and one of the junctions is kept at a higher temperature than the other, as shown in Fig. 11, an E.M.F. is set up, which causes a current to flow in the circuit, as indicated by the deflection produced in a galvanometer G included in the circuit. Seebeck was the first, in 1821, to discover this phenomenon, which is hence known as *Seebeck effect*. The arrangement is called a *thermocouple* and the E.M.F. developed a *thermo-e.m.f.* Tait investigating the dependence of the thermo-e.m.f. on the temperatures of the junctions found that the thermoelectric power is a linear function of the temperature difference between the junc-

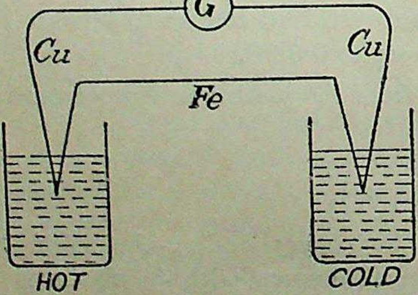


Fig. 11. Thermocouple.

tions to a first approximation and within a particular limit (the neutral temperature) depending on the metals chosen for the couple. Since the time of this discovery attempts have been made to construct thermometers based on this principle, but the chief difficulties encountered have been the choice of suitable metals that can stand high temperatures without getting oxidised and of proper insulation at such high temperatures. At the actual hour, thermoelectric thermometry has attained a degree of precision inferior to platinum resistance thermometers below 1000°C, but for higher temperatures it has become a more sensitive and convenient device.

A thermoelectric thermometer involves the following essential points :—

(1) *The choice of two suitable elements forming the thermocouple.* This is chiefly determined by the temperature to be measured. Up to about 300°C, copper-constantan and iron-constantan are found very good, since they give rise to a comparatively large e.m.f. of about 40 to 60 microvolts per degree temperature difference between the junctions. For higher temperatures, these base metals get oxidised and hence cannot be used. Iron-nickel can be used up to 600°C, and nickel-nichrome up to 1000°C, but above that, platinum and an alloy of platinum with rhodium or iridium are used up to 1600°C. Iridium and an alloy of iridium rubidium can be used in the range 1600—2000°C and tungsten-molybdenum between 2000°C and 3000°C. Although the e.m.f. developed in these noble metal couples is rather small, of the order of 5 microvolts per degree, they are usually employed nowadays for scientific work.

(2) *The electrical insulation of the wires.* This has to be attended to chiefly near the hot junction. It is done by the use of capillary glass or fireclay tubes.

(3) *The measurement of the e.m.f. developed in the circuit.* The method used depends on the accuracy desired. For very accurate work a sensitive potentiometer is used, which can measure to 0·1 microvolt, that corresponds to 0·025°C difference between the junctions for a copper-constantan couple. If only moderate accuracy is required, a high resistance unipivot dial galvanometer, which can be even calibrated to read directly temperature, is sufficient for the purpose.

(4) *The calibration of the thermocouple.* Keeping the cold junction in melting ice, and heating the hot junction to different temperatures determined by a constant volume hydrogen thermometer, the e.m.f. at each temperature is measured. A calibration curve is drawn

plotting the e.m.f. against temperature. Then the temperature of any body can be readily found from the graph when the e.m.f. of the couple with its hot junction in contact with the body is measured. It must be remembered, however, that the nature of variation of e.m.f. at different ranges of temperature must be taken into account in calibrating the thermometer. Thus, for a Pt—Pt-Rh couple, three different relations have to be used for different ranges as shown below :

From 0°C to 400°C, $E = at + b\,(1 - e^{ct})$

From 300°C to 1200°C, $E = at + bt + ct^2$

From 1100°C to 1750°C, $E = -\,a + bt + ct^2$

where t is the temperature of the hot junction a, b and c are constants having different values in the three cases, which have to be experimentally determined.

2. Description of thermoelectric thermometers. The hot junction A, which is formed by welding together electrically one end of both of the two wires chosen as the elements of the thermocouple, is contained in a tube B of porcelain, quartz or hard glass, depending on the temperature for which the thermometer is to be used (Fig. 12). The portions of the wires near the hot junction are insulated with capillary tubes C of fireclay or hard glass. The two elements are passed through mica discs D closely fitted in the outer protecting tube and are attached to terminals T T fixed on the cap closing the mouth of the tube. To these terminals are connected long, flexible leads, usually of the same material as the elements, which form the cold junction immersed in melting ice at 0°C at a fairly distant place.

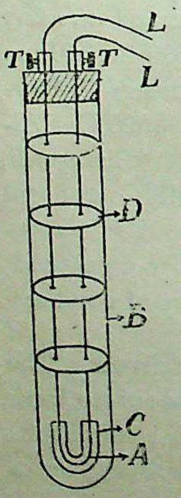


Fig. 12.
Thermoelectric thermometer.

To use the thermoelectric thermometer for measuring temperature with the greatest possible precision, a sensitive potentiometer capable o reading in microvolts is required. This can be arranged in a simple manner as follows. Two dial resistance boxes P and Q are connected in series with a potentiometer wire AB which is 1 metre long and exactly 1 ohm in resistance, an accumulator Ac, a tap key K and a thick wire rheostat Rh, as shown in Fig. 13.

The potentiometer wire is first calibrated to read accurately to 1 microvolt. For this purpose a standard cadmium cell C (1·0183 volts) is connected, along with a galvanometer, G, to the above arrangement, the positive terminal of the cell to the positive end of the resistance box Q and the negative terminal to the negative end B of the potentiometer wire [Fig. 13 (*a*)]. A resistance of 1017·3 ohms is introduced in Q and the resistance in P is so adjusted that the galvanometer shows no deflection, using the rheostat, if necessary. This means that a resistance in Q and AB, equal to 1018·3 ohms, has a fall of 1·0183 volts. Hence the potential fall in the wire AB of 1 ohm = 1·0183/1018·3 = 10^{-3} volt. Since the length of AB = 100 cms., the fall of potential per mm. is 10^{-6} volt, *i.e.*, 1 microvolt.

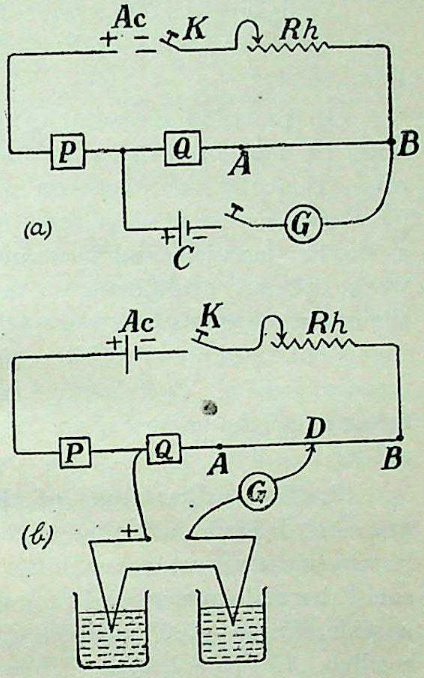


Fig. 13. Sensitive potentiometer for measuring the e.m.f. of a thermocouple.

To measure the e.m.f. developed in the thermoelectric thermometer, after having transferred the resistance in Q to P, the cadmium cell is replaced by the thermometer, taking care that the positive terminal of the thermometer leads is connected to the positive end of Q [Fig. 13 (*b*)]. To do this properly, the thermocouple circuit alone is first closed and the deflection in the galvanometer G is noted ; then the potentiometer circuit is closed and if the deflection is found to decrease, the connections are all right ; otherwise interchange the connections of thermometer leads with the potentiometer. Next the balance point D on the potentiometer wire is found when there is no deflection in the galvanometer. It may be necessary to introduce some fresh resistance (a few ohms) in Q in order to get balance on the wire ; in such a case the same amount of resistance must be removed from P, so that the total resistance in P and Q is always kept constant and the calibration is thus left undisturbed. Supposing that in obtaining D as the balance point X ohms have been introduced in Q and the length AD is l cms., the e.m.f. of the thermocouple is

$(X \times 10^{-3} + l \times 10^{-5})$ volts. Since the balance point can be determined accurate to a mm., the e.m.f. is measured to a microvolt.

To deduce the temperature from the value of e.m.f. thus experimentally determined a calibration curve is usually supplied with the thermometer.

In precision measurements, the junction of the thermometer must be kept in melting ice to avoid corrections which otherwise arise. The chief sources of error in thermoelectric thermometers are :— (*i*) Parasitic e.m.fs. developed in the circuit due to Peltier effect at the two junctions and Thomson effect along the wires of the couple whose ends are at different temperatures. These are eliminated by the use of materials free from such effects. (*ii*) Cold junction error, if it is not maintained at 0°C. (*iii*) Leakage from the light mains or furnace circuits. Such leakage currents passing through the potentiometer affect the balancing and hence have to be detected and corrected for.

3. The advantages of the thermoelectric thermometer are :—(*i*) It is specially adopted for giving continuous records of rapidly varying temperatures as in the cooling of alloys, on account of its small thermal capacity and the consequent negligible lag. (*ii*) It has a wide range, —200°C to 1600°C. (*iii*) It can be easily made direct reading. (*iv*) Simple type of thermocouples are often used for laboratory work, as they are cheap and can be easily constructed.

The chief drawbacks are :—(*i*) It is not capable of such accurate measurements as the platinum resistance thermometer at corresponding ranges. (*ii*) There is no one theoretical formula which can be utilised over a wide range and consequently every thermoelectric thermometer requires special and frequent calibration. (*iii*) The existance of a neutral temperature may also limit the range of utility.

SCALES OF TEMPERATURE

We have seen above in several places that different types of thermometry lead to different scales of temperature, so that all the scales used in practice are arbitrary in nature. We may now consider a little what is meant by a scale of temperature and why different scales disagree.

In the construction of an instrument to measure temperature, having defined the fixed points, a scale of temperature has to be devised which will enable temperature to be measured within and outside the range of the fixed points. For this purpose any property of matter which depends on the thermal state of matter, such as the expansion of solids and liquids, the pressure and volume changes of gases, the resistance variation of metals, the e.m.f. of a thermocouple etc., is used. Let the magnitudes of the property chosen be x_{ice} and x_{steam} at the lower and upper fixed points respectively. Then if its magnitude is x_t at some other temperature, the numerical value t of that temperature is given by the relation

$$\frac{t}{100} = \frac{x_t - x_{ice}}{x_{steam} - x_{ice}}$$

This is the basis of the scale of temperature. It defines any temperature at which the property used still persists. It also implies that the temperature is so defined that it varies uniformly with the chosen property.

Selecting another property of matter, the scale of temperature can be defined by a relation similar to the one given above. But it is not necessary that the two scales of temperature should agree except at the two fixed points, since the different properties of matter have little connection with one another. As a matter of fact, mercury, constant volume hydrogen and platinum scales all disagree to a greater or less extent with one another. Although the discrepancy may not be very marked within the fixed points, it becomes appreciably great at higher temperatures.

Given this inherent disagreement between the different scales of temperature and the consequent arbitrary nature of all the scales, the best way to overcome this difficulty, in practice, is to select whichever scale is most convenient as the standard and calibrate all the temperature measuring instruments with reference to it. We have mentioned already that the standard thus chosen is the constant volume hydrogen scale. This is, because there are reasons to believe that all gas scales agree at infinitely low pressure among themselves as well as with the perfect gas scale. Hence a scale of temperature based on the behaviour of gases at infinitely low pressure is less arbitrary than the mercury scale, for instance, since it depends on a property common to all gases and not on the property of one particular gas. And the hydrogen scale is perferred to all others, because it satisfies best the condition stated above.

Even with the hydrogen scale as standard, we are still left with an arbitrary scale of temperature and one cannot be satisfied until one has found *a scale independent of the properties of any particular material substance.* As we shall see in the Chapter on Thermodynamics, Lord Kelvin, from considerations of heat-engines, has developed such an *absolute scale.* It will be proved there that the ratio of two temperatures on the absolute thermodynamic scale is equal to the ratio of the two temperatures as determined on the perfect gas scale. Hence, if the zeros of the two scales are made to agree, the perfect gas scale will be identical with the thermodynamic scale at all ranges. Thus a very knotty problem concerning thermometery has been happily solved.

On account of the many difficulties involved in the practical realisation of the thermodynamic scale, the International Committee in 1927 found it necessary to adopt a practical scale known as the *International Temperature Scale.* It agrees with the absolute scale as closely as our present knowledge permits. It is also easily reproducible with accuracy, as it is based upon a number of reproducible fixed points. Numerical values are assigned to such points and the intermediate temperatures are defined by agreement as follows :—

(*a*) From −190°C to 0°C, — the platinum resistance thermometer giving temperature according to the relation

$$Rt = R_0[1 + \alpha t + \beta t^2 + \gamma(t - 100)t^3],$$

where the four constants R_0, α, β and γ are determined by calibration at ice, steam, sulphur and oxygen points.

(*b*) From 0°C to 660°C,—the platinum resistance thermometer calibrated at ice, steam and sulphur points.

(*c*) From 60°C to 1063°C,--the platinum—platinum-rhodium thermocouple giving temperature according to the formula

$$E = a + bt + ct^2,$$

where the three constants a, b and c are determined by calibration at the freezing point of antimony, the silver point and the gold point.

(*d*) Above 1063°C,—the optical pyrometer calibrated at the gold point.

QUESTIONS

1. What are the avoidable errors in mercury-in-glass thermometers and how are they corrected for ? (*Madras University*)

2. Discuss the advantages of using one of the permanent gases as a thermometric substance for defining a scale of temperature. Describe some convenient and accurate form of gas thermometer, explain its mode of use and show how the temperature is calculated from the observation made with it. (*Madras University 1925*)

3. What is an air thermometer ? Explain the method of measuring temperature by Callendar's compensated air thermometer. Describe the method of measuring very high temperatures. (*Allahabad Univerity 1927*)

4. Describe the Callendar's compensated thermometar and explain how temperatures are taken with it.
(*Madras University ; Allahabad University 1944 : Utkal University 1952 ; Punjab University 1954*)

5. Give an account of the chief methods for the determination of temperatures. Illustrate your answer by considering their applicability in the neighbourhood of 50°, 500° and 1500°C. (*Madras University*)

6. Name the various thermometers which can be used to measure temperatures near 1500°C. Describe the instrument you think more suitable, giving reasons for your choice. (*Delhi University 1956*)

7. Describe the relative merits of thermoelectric and platinum resistance methods of measuring temperatures. (*Madras University*)

8. Describe various methods of measuring high temperatures.
(*Allahabad University 1931, 1932, 1949 ; Gujerat University 1951 ; Punjab University 1956*)

9. Explain the principles underlying the different temperature measuring instruments. Describe the construction and use of the platinum resistance thermometer. (*Madras University*)

10. Give an account of the construction and use of the platinum resistance thermometer, pointing out any special advantages of the instrument.
(*Utkal University 1950 ; Gujerat University 1951 ; Punjab University 1956*)

11. State with reasons, the type of temperature measuring device which you consider most suitable for use at temperatures of : (*a*) – 260°C, (*b*) – 50°C, (*c*) 50°C, (*d*) 700°C, (*e*) 2000°C. (*London B. Sc.*)

12. Describe two methods of measuring high temperatures. State clearly the principles underlying them and the range and sensitivity of each.
(*Allahabad University 1941*)

13. Write a short essay on the measurement of (*a*) high and (*b*) low temperatures. (*Delhi University 1954 ; Punjab University 1946*)

14. In what respects is a constant volume gas thermometer superior to the constant pressure gas thermometer and the mercury-in-glass thermometer. Describe the construction and use of the international standard hydrogen constant volume thermometer.
(*Madras University ; Patna University 1949 ; Utkal Univesity 1954*)

15. Give a full and critical account of Harkar and Chappius constant volume gas thermometer.

The pressure of the air in a constant volume gas thermometer is 80 cms. and 109·3 cms. at 0°C and 100°C respectively. When the bulb is placed in some hot water the pressure is 100 cms. Calculate the temperature of the hot water. (*Patna University 1946*)
(**Ans. 63·8°C**).

16. When the bulb of a constant volume gas thermometer is placed in melting ice, the level of mercury in the open tube is 5 cms. below the level in the closed limb. When the bulb is at 273°C, the level in the open limb is 65 cms. high. Calculate the barometric pressure. (Ans. 75 cms.) (*Madras University*)

17. What is meant by a scale of temperature ? On what does the definition of any particular scale depend ?

Give detailed account of the experiment you would perform to determine the temperature of boiling aniline on the platinum resistance scale of temperature. (*Cambridge*)

18. Describe the platinum thermometer and discuss its special merits. How is it calibrated ? (*Tripos*)

19. Write notes on :

(*i*) the Beckmann thermometer (*Madras University*)

(*ii*) the maximum and minimum thermometer (*Madras University*)

(*iii*) the absolute scale of temperature. (*Delhi University 1956*)

CHAPTER II

THERMAL EXPANSION

Introduction. It is a matter of common experience that bodies change in size when they are heated. In most cases, the size increases with rise of temperature, the notable exception being water and some aqueous solutions between 0° and 4°C. This thermal expansion takes place in all bodies and in all the three states of matter, solid, liquid and gas, although its amount is different for different bodies and states. In general, gases expand more than liquids and liquids more than solids when heated to the same extent. Further, in the case of solids, since they have a shape, expansion in length, area and volume is to be expected. For liquids and gases, since they have no shape of their own, only volume expansion is to be considered; but in the case of gases, as their volume depends not only on temperature but also on pressure, two kinds of expansion, *viz.*, change of volume under constant pressure and change of pressure under constant volume, have to be dealt with. Thermal expansion, being the most common effect of heat, has naturally many practical applications; measurement of temperature is one of them as we have seen in the last chapter; there are others which we shall indicate in this chapter. Intense and detailed researches have, therefore, been made on this property of heat and the results obtained have been utilised in several fields of human activity. For the sake of clarity we shall study the expansion of solids, of liquids and of gases under separate heads.

EXPANSION OF SOLIDS

In studying the expansion of solids it is useful to distinguish two kinds of bodies, *viz.*, *isotropic* and *anisotropic*. For isotropic bodies, whose properties are the same in all directions, the expansion also is the same in all directions. To this class belong (*i*) *metals*, which though polycrystalline in nature, have their *average* properties independent of direction, due to the fact that a large number of microcrystals of which they are composed are oriented at random, (*ii*) *amorphous solids* like glass, and (*iii*) *regular systems of crystals* like rock salt. In anisotropic bodies, such as many crystals, the expansion is different in different directions; some of them, while expanding in one direction, contract in the perpendicular direction. We shall first deal with isotropic solids and then consider briefly anisotropic solids.

ISOTROPIC SOLIDS

1. Coefficients of expansion. Since solids have a definite shape, their expansion can be considered in terms of their length—*linear expansion*, area—*superficial expansion* and volume—*cubical expansion*. As different materials expand to different extents for the same rise of temperature, we need to define some quantity which will be a measure of the expansion of a given material independent of the size or shape of any particular specimen of it and hence differentiate between various materials. The quantity chosen is called the **coefficient of linear expansion** and is defined as the *ratio of the increase in length of a solid per degree rise of temperature to its original length.*

If l_1 and l_2 are the lengths of a rod at two temperatures t_1°C and t_2°C, the coefficient of linear expansion α of the rod is given by the relation

$$\alpha = \frac{l_2 - l_1}{l_1(t_2 - t_1)} \qquad \text{... (1)}$$

$$\text{Or} \qquad \alpha l_1(t_2 - t_1) = l_2 - l_1$$

$$\therefore \quad l_2 = l_1 + \alpha l_1(t_2 - t_1) = l_1\{1 + \alpha(t_2 - t_1)\}$$

If l_0 is the length of the rod at 0°C and l_t at a temperature t°C, then we have

$$l_t = l_0(1 + \alpha t) \qquad \text{... (2)}$$

This is the form in which the coefficient of linear expansion is often expressed. It fits experimental facts for the temperature range 0° to 100°C. But for much wider ranges, say from −200°C to 600°C, it is found that the expansion is no longer uniform; the increase in length for a given rise in temperature becomes greater, the higher the temperature. Hence the more general relation connecting length and temperature has to be used which is of the form

$$l_t = l_0(1 + \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3 + \ldots\ldots) \qquad \text{... (3)}$$

where α_1, α_2, α_3 are constants which decrease rapidly. This non-linear relation is purely empirical, for which no satisfactory theoretical explanation can be had as yet. Since α itself is a very small quantity of the order of 1/10,000, one can be content with relation (2). Further, for all practical purposes, the coefficient of linear expansion may be considered as independent of the initial temperature, so that relation (1) may be used in the experimental determination of that quantity.

Coefficient of superficial expansion is defined as the *ratio of the increase in area of the solid per degree rise of temperature to the original area.* If a_1 and a_2 be the areas of a solid at t_1°C and t_2°C respectively, then the coefficient of superficial expansion β is given by

$$\beta = \frac{a_2 - a_1}{a_1(t_2 - t_1)} \qquad \ldots (4)$$

Considering a square plate with sides of unit length, if the temperature of the plate is raised by 1°C, each side will increase in length by a quantity α, which is the coefficient of linear expansion. The new area will be $(1 + \alpha)^2$ or $1 + 2\alpha$, neglecting higher powers of α, since it is small. Hence, using relation (4)

$$\beta = \frac{(1 + 2\alpha) - 1}{1 \times 1} = 2\alpha \qquad \ldots (5)$$

Thus *the coefficient of superficial expansion is double the coefficient of linear expansion.*

Coefficient of volume expansion is defined, in a similar manner, as *the ratio of the increase in volume of the solid per degree rise of temperature to the original volume.* If v_1 and v_2 be the volumes of the solid at t_1°C and t_2°C respectively, then the coefficient of volume expansion γ is given by

$$\gamma = \frac{v_2 - v_1}{v_1(t_2 - t_1)} \qquad \ldots (6)$$

Considering a cube of side of unit length whose temperature is raised through 1°C, its volume becomes $(1 + \alpha)^3$ or $1 + 3\alpha$, neglecting higher powers of α. Hence, from (6)

$$\gamma = \frac{(1 + 3\alpha) - 1}{1 \times 1} = 3\alpha \qquad \ldots (7)$$

Thus *the coefficient of volume expansion is thrice the coefficient of linear expansion.*

Expansion and density. Since the volume of a solid increases on heating while its mass remains constant, its density must proportionately diminish. Let a solid of mass m grm. have volumes v_1 and v_2 and densities d_1 and d_2 at temperatures t_1°C and t_2°C respectively. Then we have

$$m = v_1 d_1 = v_2 d_2$$

or $$\frac{v_2}{v_1} = \frac{d_1}{d_2}$$

But $$v_1 = v_0(1 + \gamma t_1)$$

and $$v_2 = v_0(1 + \gamma t_2),$$

where v_0 is the volume at 0°C and γ the coefficient of cubical expansion of the solid. Hence

$$\frac{d_1}{d_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1} = 1 + \gamma(t_2 - t_1),$$

since $1/(1 + \gamma t_1)$ can be replaced by $(1 - \gamma t_1)$.

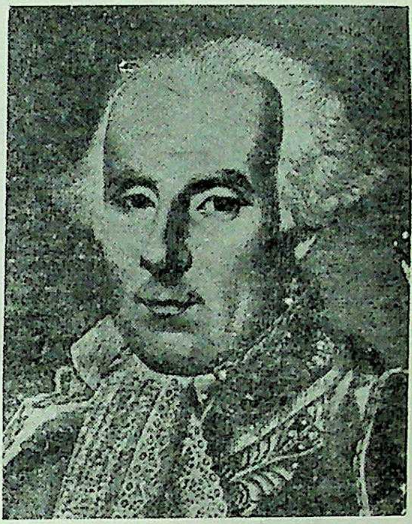
$$\therefore \qquad \gamma = \frac{d_1 - d_2}{d_2(t_2 - t_1)} \qquad \ldots (8)$$

The simple relations (5) and (7) are useful, since, in practice, α is more easily and more accurately determined than β or γ. Knowing α, the other two constants are readily estimated. Hence experiments on the expansion of solids generally consist in measuring the linear expansion of rods of the solid.

2. Experimental determination of the coefficient of linear expansion. As the coefficient of linear expansion is a very small quantity, in its experimental determination it becomes necessary, in the first place, to use a conveniently *long rod* and heat it through a fairly *large range of temperature*. Even thus the increase in length to be measured still remains a small quantity : a metal rod one metre long when heated through 100°C increases in length by about 1 mm. To measure such small changes in length accurately, delicate measuring instruments or special devices of magnification have to be employed. The problem becomes still more difficult when the solid can be had only in small bits of about 1 cm. in length, as in the case of many crystals.

Mechanical and optical levers have been employed to magnify the expansion ; micrometer screws and microscopes have been used to measure directly the small expansion. But the modern standard methods are either *comparator* or *interferometer* methods. The experiments described below serve well to illustrate how scientific research, in general, is conducted, new techniques striving to overcome the defects of older ones and thereby achieve greater precision in measurements and better results.

(*i*) *Mechanical lever method.* Laplace and Lavoisier were the first to employ the lever principle for magnifying the very small thermal expansion of solids. The device used was to convert the change in length into a change in angle by means of a lever arrangement and measure the angular change with a scale and telescope. Their apparatus is shown in Fig. 14. One end A of the experimental rod is fixed, while the other end B pushes against a vertical lever BO. A telescope TT is fixed to the top of the lever, pivoted at O, and focused on a distant vertical scale S. The rod AB is first placed in a bath of melting ice and the scale of division E seen through the telescope is noted. The rod is then enclosed in a hot bath maintained at a constant high temperature. The free end B of the rod expands to a point C and thereby tilts the telescope to a new position T′T′. In consequence a new scale division F is seen through the telescope. The actual small expansion BC of the rod is obtained from the relation.



Laplace

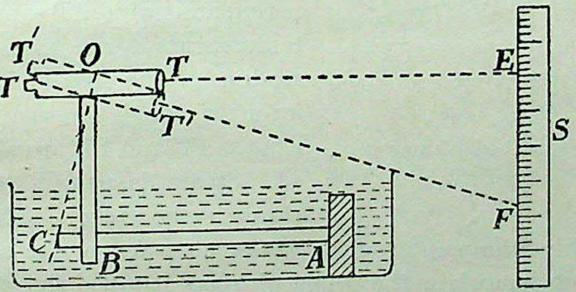


Fig. 14. Apparatus of Laplace and Lavoisier.

$$BC = BO \tan \angle BOC = BO \tan \angle EOF = BO \times (EF/OE)$$

Since BO, OE and EF can be measured, BC is determined with fair accuracy by the magnifying device employed.

The coefficient of linear expansion α of the material of the rod is given by

$$\alpha = \frac{BC}{l \times t} = \frac{BO \times EF}{OE \times l \times t}$$

where l is the length of the rod at 0°C and t the temperature of the hot bath.

This method is ordinarily adopted, with certain modifications, to measure α of solids in the form of a wire. A wire AB, about a metre long, is clamped rigidly at the upper end (Fig. 15) and carries a weight W at the lower end to keep it taut. A long, light and straight wooden strip L, pivoted at P, is attached to the wire at C; its free end acting as a pointer moves over a vertical scale S. The wire is enclosed in a steam jacket J with three openings, the top one for letting in steam, the bottom one for letting out steam and the middle one for inserting a thermometer T to read the temperature inside the jacket.

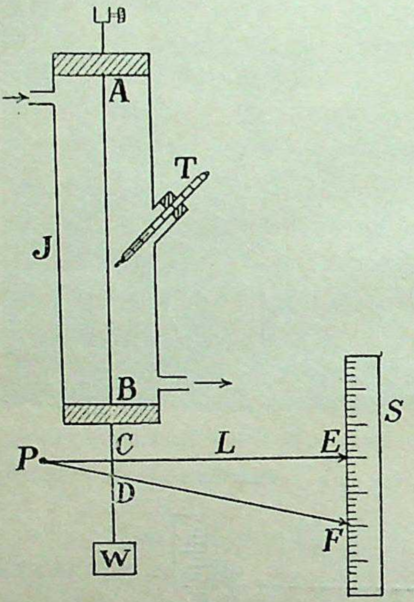


Fig. 15. Lever method of measuring coeff. of linear expansion of a wire.

The initial length l of the experimental wire AB and its initial temperature t_1 are measured. The reading of the free end E of the lever is noted on the scale; the lengths PC and PE are also measured. Steam is passed continuously through the jacket. The wire expands, making the pointer of the lever move down the scale. After a fairly long time when the whole wire has attained the temperature of steam, as indicated by the steady reading of T, the pointer remains steady at a point F on the scale. The temperature t_2 of steam as well as the reading of F are recorded.

The actual increase in length of the wire is CD which can be estimated as follows :—

From similar triangles we have,

$$\frac{CD}{EF} = \frac{PC}{PE} \text{ or } CD = \frac{PC}{PE} \cdot EF$$

Since PC, PE and EF are known, CD is readily found.

The coefficient of linear expansion α of the material of the wire is given by

$$\alpha = \frac{CD}{l(t_2 - t_1)} = \frac{PC \times EF}{PE \times l(t_2 - t_1)}$$

(*ii*) *Optic lever method.* This is an improvement over the previous method, since by the use of an optic lever in the place of a mechanical lever, the magnification is doubled due to the basic principle of the optic lever, *viz.*, when a mirror is tilted through a certain angle, the reflected ray is shifted through double that angle, the direction of the incident ray remaining unchanged. Hence this method is bound to give results of greater accuracy and is often used as an accurate laboratory method of determining the coefficient of linear expansion of solid rods.

The optic lever consists of a small plane rectangular metallic plate P mounted on three pointed legs ; two of these legs R and S are situated on the same line at one end of the plate while the third T is arranged at the other end on the perpendicular bisector of the above-mentioned line. A small piece of plane mirror M is fixed on the top surface of the plate in a vertical position and just above the two legs R and S. (Fig. 16).

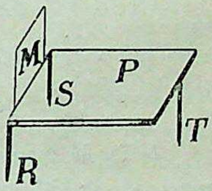


Fig. 16. Optic lever.

The experimental rod AB fixed vertically on a board is enclosed in a steam jacket J. (Fig. 17). The lower end A of the rod being fixed, expansion can take place only in the upward direction. The top end B protrudes slightly through the cork closing the top of the steam jacket. The front leg of the optic lever rests on top end of the rod, while the hind legs rest on a fixed platform. A vertical scale and telescope are arranged in front of the mirror at a distance of about a metre.

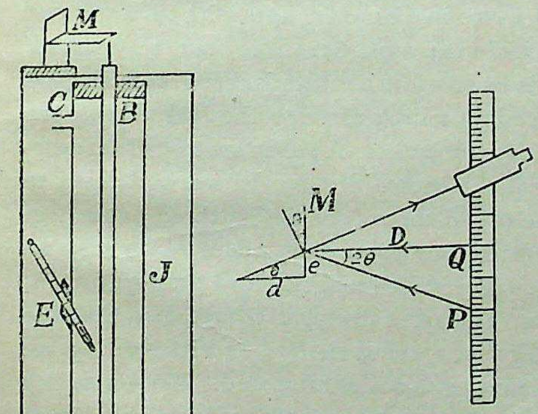


Fig. 17. Optic lever method.

The initial length l and initial temperature t_1 of the rod are recorded. The telescope is focused on the image of the scale seen by reflection in the mirror and the reading P corresponding to the horizontal cross-wire is noted. Steam is passed through the jacket for a sufficiently long time so as to allow the rod to attain the steady temperature t_2 of steam. Then the thermometer is read and the new scale reading Q is taken.

As the rod expands, the lever and its mirror are tilted through an angle, say θ, so that the reflected ray turns through an angle 2θ. If D is the distance between the scale and the mirror,

$$2\theta = \frac{PQ}{D} \text{ or } \theta = \frac{PQ}{2D}$$

If e is the increase in length of the rod and d the perpendicular distance between the front leg and the line joining the back legs,

$$\theta = \frac{e}{d}$$

Hence $e = \theta.d = \dfrac{PQ.d}{2D}$

The coefficient of linear expansion α is given by

$$\alpha = \frac{e}{l(t_2 - t_1)} = \frac{PQ.d}{2D.l(t_2 - t_1)}.$$

(*iii*) *Micrometer method*. Since an ordinary micrometer screw can read to 0·002 mm., in earlier measurements of linear expansion, a spherometer was used to determine directly the increase in length.

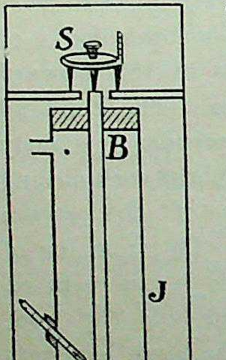


Fig. 18. Micrometer method.

The experimental rod AB, about a metre long and 1 cm. in diameter, rests with its lower end A fixed, while the upper end B is free to expand. The rod is enclosed in a steam jacket J with the top end protruding a little through the cork closing the top of the steam jacket. A spherometer S is arranged so that the central leg can be screwed down to touch the top of the rod, while its three outer legs are supported on a glass plate mounted on a stand (Fig. 18). The initial length l and temperature t_1 are taken. The spherometer is adjusted so that the central leg just touches the rod and its reading on the head and pitch scales are noted. The central leg is then raised, steam is passed through the jacket until the temperature t_2 is constant. The spherometer is again adjusted for its central leg to touch the rod and its reading taken. The difference between the two readings of the spherometer gives the increase in length e of the rod. The coefficient of linear expansion is given by

$$\alpha = \frac{e}{l(t_2 - t_1)}$$

The chief difficulty in this method is to set the spherometer both in the initial and final stages with the same degree of accuracy. The ordinary method of adjusting the spherometer by the sense of touch does not permit such accurate setting. This drawback can be overcome in a simple manner by the use of an electrical circuit formed with the rod, spherometer, a galvanometer and a battery, so that, when the central leg just touches the rod, the galvanometer is deflected. But more ingenious devices have been employed which will be described in the following methods.

(*iv*) *Roy and Ramsden's method.* Three bars X, Y, Z, of which X and Z are standard ones of any suitable material and Y the experimental one, are placed horizontally in three troughs. The troughs are arranged parallel to each other, with the one containing Y between those having X and Z. X carries two cross-wires CC, one at each end, Y two object glasses OO, and Z two eye-pieces EE in a similar manner, (Fig. 19). The two sets of cross-wires, object glasses and eye-pieces arranged on uprights fixed to the bars are aligned in such a way as to form two microscopes. The objectives carried by the central experimental bar can be moved along the length of the bar by means of two micrometer screws not shown in the figure.

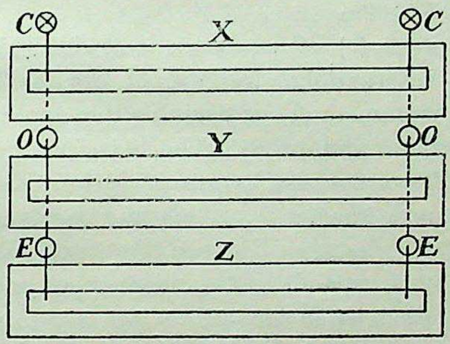


Fig. 19. Apparatus of Roy and Ramsden.

The three troughs are filled with melting ice. The eye-pieces are focused on the respective cross-wires through the objectives. The distance between the centres of the two cross-wires represents the length of the bar whose coefficient of linear expansion is to be determined. The melting ice in the central trough is replaced by oil which is heated to a convenient constant temperature, while the outer troughs contain melting ice during the whole of the experiment, since the standard bars in them carry the "reference lines" and hence must be kept constant in length throughout. Due to expansion of the central bar, the object glasses carried by it will have moved out of line. By working on the micrometer screws, the object glasses are shifted again into line of vision and the coincidence restored. The sum of the distances through which the micrometer screws have been moved gives the increase in length of the bar. The coefficient of linear expansion of the bar is readily calculated, knowing the temperature of the oil-bath.

In this method the difficulty of setting the micrometer screw with the same degree of accuracy, mentioned in the previous experiment, is overcome by observing the coincidence of the image of the cross-wires with those in the eye-piece of a microscope. Roy and Ramsden were able to measure the linear expansion of bars with a great degree of accuracy, although their method is mainly of historical interest and has been replaced by the following most modern method.

(*v*) *Comparator method.* This method devised by the Bureau International des Poids et Mesures, is considered as a standard precision method for studying the expansion of materials in the form of bars and tubes. The *principle* involved may be stated as follows: Two fine marks are made on the experimental bar. A standard metre bar, always kept at a constant temperature, is used to measure the distance between the two marks, which varies as the bar under test expands. Two microscopes provided with micrometer eye-pieces or micrometer screws are used in the comparative estimation of expansion. Hence the method is known as 'comparator method'.

Experimental details. The bar under test with two fine marks XX at a decent distance apart and a standard metre are mounted

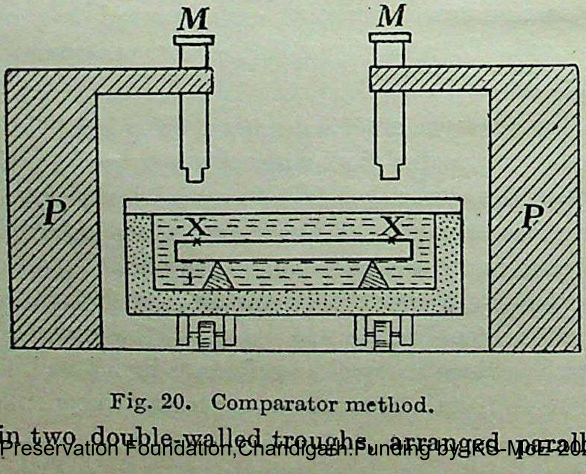


Fig. 20. Comparator method.

horizontally in two double-walled troughs, arranged parallel to each other. The troughs are fixed in a platform running on rails, so that either the bar or the standard metre can be brought into the field of view of two microscopes MM mounted vertically in massive stone pillars PP. The two troughs are first filled with water surrounded by melting ice in the space between the double walls. The standard metre is brought underneath the microscopes. These are adjusted using the micrometre screws until two lines of graduation on the metre, approximately the same distance apart as the marks on the other bar, are in coincidence with their vertical cross-wires. Next the experimental bar is wheeled into position and the microscopes are set on its marks. From the change in the micrometer readings, the length of the bar at 0°C is readily found. The melting ice in the outer compartment of the trough is then replaced by water which is heated under thermostatic control, so that the bar can be maintained constant at any desired temperature. The microscopes are again set and read. The expansion of the bar at any given temperature is equal to the sum of the differences in the readings of the two micrometers used for setting the microscopes on the marks at that temperature, which is read from accurate standard thermometers inserted in the trough, after stirring the water well by special turbine arrangement. The process is repeated for different temperatures so that the expansion can be studied over a wide range of temperature. For measurements at low temperature the bar is immersed in liquid air. Thus the coefficient of linear expansion of the bar can be determined for different temperatures and its variation, if any, can also be estimated.

During the whole of the experiment, the trough having the standard metre contains melting ice, so that it is kept at a constant temperature, 0°C. At the end, this trough is railed under the microscopes and the microscopes are adjusted again, in order to see whether the micrometer readings are the same as at the beginning. If they are different, the standard length of reference has been altered in the course of the experiment due to radiation of heat and appropriate corrections must be made for this source of error. It is to reduce this very small correction that the microscopes are mounted on massive stone pillars of large thermal capacity.

It may be noted that in this method the difficulty of setting the micrometer screw to the same degree of accuracy referred to in method (*iii*) is eliminated by observing the coincidence of the image of a fine mark on the bar with a cross-wire of a vertical microscope.

(*vi*) *Interference method.* This is an optical method depending upon the observation of interference fringes, which is capable of very great accuracy, since it can measure expansions of the order of 10^{-6} cm. It is particularly suited for substances which can be obtained only in small bits, as in the case of crystals.

Fizeau was the first to devise the method for measuring the expansion of crystals. Since then, many modifications and adaptations have been made to his technique, so that today the method has become most satisfactory chiefly in the study of dilatation of crystals. After stating the principle of the method, we shall describe first Fizeau's historical experiment and then the modern adaptations.

The *principle* of the method is based, as in the study of Newton's rings in Optics, upon the interference of light by multiple reflection in thin air films. Light incident on such a film suffers successive reflections at the surfaces that limit the film and moves backwards and forwards within the film. These reflected rays interfere, reinforcing each other if their path difference is an even multiple of half the wavelength of the light used and annulling each other if the path difference is an odd multiple. This gives rise to successive dark and bright bands, governed by the general relations

$$\delta = 2\mu e \cos r = 2n\lambda/2 \ldots\ldots\ldots\ldots \text{(dark bands)}$$

$$= 2\mu e \cos r = (2n + 1)\lambda/2 \ldots \text{(bright bands)}$$

where δ is the path difference, μ the refractive index of the material of the film, r the angle of refraction of the ray into the film, e the thickness of the film corresponding to the n^{th} dark or bright band and λ the wavelength of the light used. If a beam of white light is used coloured fringes will be formed, whereas with monochromatic light, the bright bands will have the colour depending on the source used, *e.g.*, yellow in the case of sodium light.

If the light is made to fall normally on the film, $r = 0$ and hence $\cos r = 1$; further, in the case of an air film $\mu = 1$. Hence the above relations are reduced to

$$\delta = 2e = 2n\,\lambda/2 \qquad \text{for dark bands}$$

$$= 2e = (2n + 1)\lambda/2 \text{ for bright bands}$$

If the order of the dark or bright band can be noted, the corresponding thickness of the film can be estimated. This fact is made use of in measuring the very small expansions. If the thickness of the air film is made to change due to thermal expansion of a specimen, the interference bands will be shifted, at the rate of one bandwidth (*i.e.*, distance between successive dark or bright bands) for every change of thickness of air-film by half the wavelength of the light used. Hence counting the number of bands displaced and knowing the wavelength of the light used, the expansion can be readily calculated.

Since the wavelength of light ordinarily employed is of the order of 6×10^{-5} cm. and a shift of $\frac{1}{5}$ of a bandwidth can be easily detected, expansions of the order of 6×10^{-6} cm. can be measured accurately by this method.

Fizeau's experiment. The crystal C under test is cut into a plate with parallel faces of a few mm. thickness. It is placed on a plane metal platform AB supported on three adjustable screws passing through it near the edges. These screws support a glass plate GG which can be adjusted to be nearly parallel and very close to the top surface of C, thereby enclosing a thin air-film in the inter-space. The bottom surface of GG and the top surface of C must be optically plane. (Fig. 21). A beam of white light is made to fall on the glass plate at normal incidence. Under these conditions coloured fringes are produced which can be observed through a microscope arranged vertically above the glass plate and focused on the air-film. It the two surfaces that enclose the air-film are exactly parallel, only certain colours will be seen but no fringes, since these are formed at infinity in such a case. But in practice, as it is not possible to make the two surfaces absolutely parallel, an air wedge of very small angle is actually formed between them and the fringes appear as very nearly straight lines formed at the film itself.

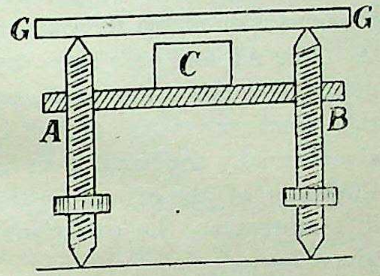


Fig. 21. Fizeau's apparatus.

The above arrangement is placed in an enclosure and heated, the temperature being controlled thermostatically. As the crystal expands, the thickness of the air-film changes by an amount equal to the difference of the expansion of the crystal and the expansion of the screws, which causes the cover-plate GG also to be displaced. Due to this change in thickness of the air-film, the fringes are displaced. Arranging the cross-wire of the microscope against a dark band, the number of bands that gradually cross it is counted until the shifting ceases when the apparatus has attained the constant temperature of the enclosure. Supposing x bands have thus been counted, we have $2e_1 = n\lambda$ and $2e_2 = (n + x)\lambda$, where e_1 and e_2 are the initial and final thickness of the air-film. Hence

$$2(e_1 - e_2) = x\lambda$$

Or $$(e_1 - e_2) = x\lambda/2$$

Since $e_1 - e_2$ is the differential expansion of the crystal and the screws, to get the expansion of the crystal alone, the experiment is repeated without the crystal, which gives the expansion of the screws to be deducted.

Tutton has been able to eliminate the effect of the expansion of the screws by means of an *aluminium compensator*. This is a plate of aluminium of such thickness that its expansion compensates for the expansion of the screws made of iridio-platinum. It is placed on the table AB and over it the crystal. Thus the amount by which the plate GG is raised due to the expansion of the screws is made up by the equal expansion of the compensator, In such a case $(e_1 - e_2)$ gives directly the increase in length of the crystal. If l be the initial thickness of the crystal (in the vertical direction) and θ the increase in temperature, the coefficient of linear expansion of the crystal is given by

$$\alpha = \frac{e_1 - e_2}{l\theta} = \frac{x\lambda/2}{l\theta}$$

In an experiment, using sodium light whose $\lambda = \cdot00005896$ cm. and a plate of rock-crystal 5 mm. thick, it was found that a displacement of 9 entire bands took place when the temperature was increased from 10° to 50°C.

The increase in length $= 9 \times \cdot00002948$ cm.
$= \cdot000261$ cm.

The coefficient of linear expansion of rock-salt

$$= \frac{\cdot000261}{\cdot5 \times 40} = \frac{\cdot000261}{20} = \cdot00001305$$
$$= 13 \times 10^{-6}$$

Thus we see that the accuracy obtained in this method is very great.

We shall now mention briefly two modern techniques based on Fizeau's method :

Newton's rings method. The apparatus used in this method is practically the same as the one of Fizeau, except the glass plate GG is replaced by a lens L, as shown in Fig. 22. Monochromatic light from a cadmium or mercury vapour lamp is first rendered parallel and then reflected vertically downwards by the glass plate P on to the air film formed between the lower surface of the lens L and the upper surface of the crystal C. By carefully adjusting the levelling screws Newton's rings are formed and observed through a microsocpe M focused on the air film. As the temperature of the whole apparatus is raised, owing to the expansion of the crystal, the thickness of the air film changes and this is accompanied by the movement of rings, which appear to expand outwards. Counting the number of rings as they move across the field of view for a given rise of temperature, the expansion of the crystal and hence its coefficient of expansion can be estimated. Corrections have to be made for the expansion of the levelling screws and the change in refractive index of air with rise of temperature. This is done by repeating the experiment under the same conditions but without the crystal in position.

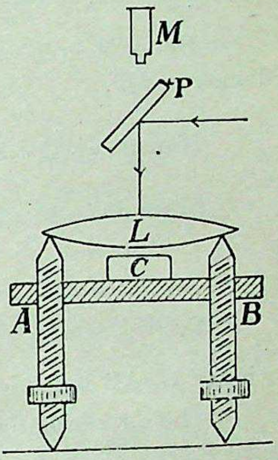


Fig. 22. Newton's rings method.

Air wedge dilatometer. In this method the specimen of the crystal is in the form of a short rod and its linear expansion is measured by a device known as an air-wedge. This consists of two optically plane glass plates AB and AC, hinged at one end A and separated by a small distance CB at the other, so that a wedge shaped film of air is enclosed between them. When light from a monochromatic source, rendered parallel, is reflected vertically down on such an air film, parallel line bands, dark and bright, are formed, which can be observed through a microscope. The special characteristics of the arrangement are the very small *angle* θ *of the wedge*, the *bandwidth* β and the distance of separation t at the open end BC. They are inter-related as follows :—

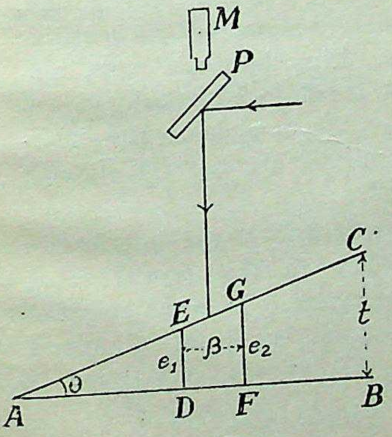


Fig. 23. Air wedge.

Considering any two successive dark bands, let the corresponding thicknesses of the air film be DE $= e_1$ and FG $= e_2$ respectively.

Then $$2e_1 = n\lambda$$

and $$2e_2 = (n + 1)\lambda$$

$$\therefore \quad 2(e_2 - e_1) = \lambda$$

Hence the difference in thickness of the air film at the two bands = $\lambda/2$.

$$\text{Now } \theta = \frac{e_1}{\text{AD}} = \frac{e_2}{\text{AF}} = \frac{e_2 - e_1}{\text{AF} - \text{AD}} = \frac{e_2 - e_1}{\text{DF}} = \frac{\lambda}{2\beta}$$

Since θ is also equal to t/AB

$$\frac{t}{\text{AB}} = \frac{\lambda}{2\beta}$$

Or $$t = \frac{\text{AB}.\lambda}{2\beta} = \frac{\lambda l}{2\beta}$$

where l = AB is the length of the wedge.

The air wedge formed between the two optically plane glass plates AB and AD is arranged on a bed plate E. A rod of the crystal C is held vertically, its top pointed end supporting the glass plate AD and its bottom end resting fixed on the bed-plate, as shown in Fig. 24. The specimen rod is wound with a heater coil, so that it can be heated to any desired temperature, which is accurately measured by a sensitive thermocouple. Monochromatic light, rendered parallel, is reflected vertically downwards to fall on the air wedge. The interference bands formed are observed through a microscope M.

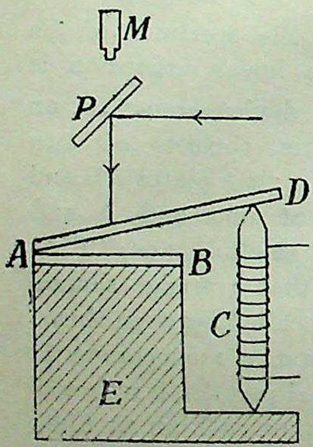


Fig. 24. Air wedge dilatometer.

The bandwidth β_1 of the interference band is found when the crystal is at the room temperature. Then the height of the air wedge h_1 at the point of support of the plate AD by the crystal rod is given by

$$h_1 = \frac{l\lambda}{2\beta_1}$$

where l is the distance between the hinge A and the point of support mentioned above.

The crystal is next heated to any required temperature. As the crystal rod expands, the height of the air wedge at the point of support will increase, and the interference pattern will, in consequence, shrink, the bands getting closer. When the specimen rod has reached the desired steady temperature, the new bandwidth β_2 is determined. The new height of the air wedge h_2 at the point of support is given by

$$h_2 = \frac{l\lambda}{2\beta_2}$$

The increase in length e of the crystal rod is therefore given by

$$e = h_2 - h_1 = \frac{l\lambda}{2}\left\{\frac{1}{\beta_2} - \frac{1}{\beta_1}\right\}$$

In order to measure β_1 and β_2 accurately two fine lines are drawn on the plate AD with a diamond pin at a distance of about a cm. or two. The microscope can be focused to view simultaneously both these two reference lines and the interference pattern. The number of bands contained between the two reference lines is counted ; the distance between the reference lines divided by the number of bands counted gives the bandwidth.

Since the increase in length of the crystal is thus accurately measured, knowing the initial length of the rod and the initial and final temperatures, the coefficient of linear expansion of the crystal can be calculated.

ANISOTROPIC SOLIDS

As already stated, crystals, in general, belong to this class, their expansion being different in different directions. Hence if a cube of a crystal is heated, the sides expand to different amounts, so that they become unequal and the *dihedral angle*, *i.e.*, the angle between any two faces ceases to be a right angle. For every crystal, however, three mutually perpendicular directions can be found, such that if a cube is cut with its sides parallel to these directions and heated, the dihedral angle remains unchanged (*i.e.*, right angles) although the sides become unequal due to different expansions. These three directions are called the *principal axes of dilatation*, which are not necessarily the same as the axes of symmetry. The linear coefficients of expansion along these three directions are known as the *principal coefficients of expansion* and may be represented by the symbols λ_1, λ_2, λ_3. Hence if a cube of side l_0 at 0°C be cut with its edges parallel to the principal dilatation axes and heated to θ°C, it becomes a parallelopiped whose edges are given by $l_0(1 + \lambda_1\theta)$, $l_0(1 + \lambda_2\theta)$ and $l_0(1 + \lambda_3\theta)$. The volume of the cube v will then be

$$\begin{aligned} v &= l_0^3\,(1 + \lambda_1\theta)\,(1 + \lambda_2\theta)\,(1 + \lambda_3\theta) \\ &= v_0\,(1 + \lambda_1\theta)\,(1 + \lambda_2\theta)\,(1 + \lambda_3\theta) \\ &= v_0\,[1 + (\lambda_1 + \lambda_2 + \lambda_3)\,\theta], \end{aligned}$$

(neglecting the products $\lambda_1\lambda_2$, etc.,) where v_0 is the original volume at 0°C.

As the *coefficient of cubical expansion* (γ) is given by

$$\gamma = \frac{v - v_0}{v_0\theta},$$

$$\gamma = \lambda_1 + \lambda_2 + \lambda_3$$

For crystals belonging to the *cubic system* as rock salt, diamond, etc., $\lambda_1 = \lambda_2 = \lambda_3$, so that *the cubical dilatation is three times the linear dilatation*. For crystals of the *uniaxial system*, there is an axis of symmetry, which is one of the principal axes, and perpendicular to which the physical properties are the same. Hence in such crystals, if λ_1 be the linear coefficient along the axis of symmetry, then the other two principal coefficients are equal *i.e.*, $\lambda_2 = \lambda_3$; but $\lambda_1 \neq \lambda_2$ or λ_3 ; thus there are only two principal coefficients λ_1 and $(\lambda_2 = \lambda_3)$. In systems which are neither cubic nor uniaxial $\lambda_1 \neq \lambda_2 \neq \lambda_3$.

The linear expansion in any other direction may be expressed in terms of the principal coefficients and the direction cosines (*i.e.*, the cosines of the angles which the direction makes with the principal axes). Let OP be the given direction, P being a particle of the crystal in that direction. Let OP be inclined at α, β, γ, respectively to the three principal axes OX, OY, OZ, and the coordinates of P referred to these axes be (x, y, z) at zero temperature (Fig. 25). At any other temperature θ, due to expansion let the particle move from P to P′. These points may be assumed to lie along the same line since the change in direction is small. Let OP $= r$ and OP′ $= r'$. Then

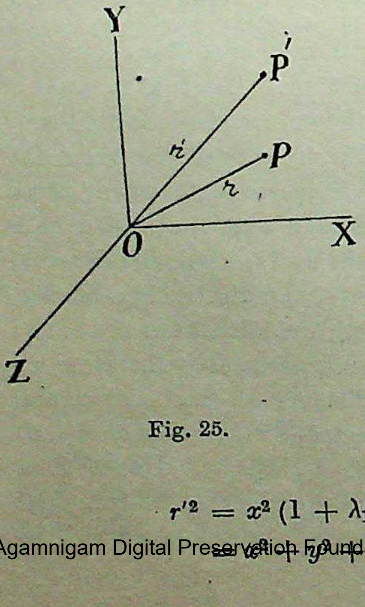


Fig. 25.

$$r^2 = x^2 + y^2 + z^2$$

$$r'^2 = x^2\,(1 + \lambda_1\theta)^2 + y^2\,(1 + \lambda_2\theta)^2 + z^2\,(1 + \lambda_3\theta)^2$$

$$= x^2 + y^2 + z^2 + 2\theta\,(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2)$$ approximately

$$= r^2 + 2\theta\,(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2)$$

$$\therefore r'^2 - r^2 = 2\theta\,(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2) \qquad \ldots (1)$$

The linear dilatation λ in the direction OP is given by

$$\lambda = \frac{r' - r}{r\theta}$$

From (1) we have $r' - r = \dfrac{2\theta}{r' + r}(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2)$

Since $r' + r$ is nearly equal to $2r$,

$$r' - r = \frac{2\theta}{2r}(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2)$$

$$\therefore \quad \lambda = 2\theta\left(\frac{\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2}{2r\,.\,r\theta}\right)$$

$$= \frac{\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2}{r^2}$$

$$= \lambda_1 \frac{x^2}{r^2} + \lambda_2 \frac{y^2}{r^2} + \lambda_3 \frac{z^2}{r^2}.$$

$$= \lambda_1 \cos^2\alpha + \lambda_2 \cos^2\beta + \lambda_3 \cos^2\gamma \qquad \ldots (2)$$

Thus the linear coefficient in any direction can be expressed in terms of the principal coefficients and the direction cosines.

Considering relation (2), the following interesting deductions can be made :—

(1) In a direction in the crystal, for which $\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2 = 0$, there can be no expansion or contraction.

(2) Along a direction equally inclined to the three principal axes, $\cos^2\alpha = \cos^2\beta = \cos^2\gamma = 1/3$. In this direction

$$\lambda = \tfrac{1}{3}(\lambda_1 + \lambda_2 + \lambda_3),$$

i.e., the linear expansion is one-third the cubical dilatation. Hence from a single measurement of linear expansion in such a direction, the cubical dilatation can be readily obtained.

(3) The sum of linear coefficients in any three mutually perpendicular directions is a constant equal to the cubical dilatation. For, let λ', λ'' and λ''' be the linear coefficients in any three mutually perpendicular directions. Then from relation (2)

$$\lambda' = \Sigma\lambda_1 \cos^2\alpha_1$$

$$\lambda'' = \Sigma\lambda_2 \cos^2\alpha_2$$

$$\lambda''' = \Sigma\lambda_3 \cos^2\alpha_3$$

$$\therefore \quad \lambda' + \lambda'' + \lambda''' = \lambda_1 (\cos^2\alpha_1 + \cos^2\alpha_2 + \cos^2\alpha_3) + \lambda_2 (\cos^2\beta_1 + \cos^2\beta_2 + \cos^2\beta_3) + \lambda_3 (\cos^2\gamma_1 + \cos^2\gamma_2 + \cos^2\gamma_3).$$

But $\cos^2\alpha_1 + \cos^2\alpha_2 + \cos^2\alpha_3$ is the sum of the squares of the direction cosines of the X-axis with the three mutually perpendicular directions, which, from trigonometry is equal to 1 ; similarly the other two terms in β and γ.

$$\therefore \quad \lambda' + \lambda'' + \lambda''' = \lambda_1 + \lambda_2 + \lambda_3 = \text{a constant}$$

The very small thermal dilatations of crystals can be measured only by the interference methods, as already described (*Cf.* pp. 52-57).

Results. The coefficients of linear expansion of solids, both isotropic and anisotropic, have values varying from $0{\cdot}5 \times 10^{-6}$ for silica glass to $31{\cdot}6 \times 10^{-6}$ for cadmium, in the range of 0 to 100°C. As already mentioned the coefficient of linear expansion of a given solid changes appreciably for other ranges of temperatures, increasing for temperatures higher than 100°C and decreasing for temperatures lower than 0°C. Hence the values usually given in tables refer to mean coefficients, which is not the same as the true coefficients given by $(1/l) . (dl/dt)$.

Grüneisen's law. Grüneisen measuring the true coefficients of a number of isotropic metals at very low temperatures has deduced an important generalisation called the Grüneisen's law. It states that the *ratio of the coefficient of linear expansion and the specific heat of a metal is a constant, independent of temperature*. This means that both the specific heat and the coefficient of expansion decrease with decrease of temperature ; but there are too may discrepancies from this law to make it theoretically significant.

Study of the expansion of silica and invar has been of some practical importance. The expansion of silica, as investigated by several workers, is very small ($\alpha = 0{\cdot}5 \times 10^{-6}$). The graph relating the coefficient of expansion and temperature is found to be a straight line between room temperature and 1000°C but bends at both ends ; the coefficient is negative below -80°C. Hence vessels made of silica can be heated to pretty high temperatures without fear of breakage. Silica glass, *i.e.*, quartz fused and resolidified into the non-crystalline state, is commonly used for making thermometer tubes. A measuring rod made of fused quartz alters very little in length even when its temperature is raised to 100°C. Sometimes fused quartz is used for the mirrors of telescopes, so that the mirrors may maintain their shapes unaltered in spite of variations in temperature.

Invar, an alloy of nickel and steel (36% + 64%), introduced by M. Guillaume, a French metallurgist, has a very small coefficient of expansion ($0{\cdot}9 \times 10^{-6}$) as compared with either nickel (13×10^{-6}) or steel (11×10^{-6}) at ordinary temperatures, whence its name "invar". It is generally used for making survey metal tapes of constant length and in the manufacture of precision clocks and watches, as we shall see below.

Some interesting results have been obtained with crystals also. The coefficient of linear expansion of quartz crystal is $7{\cdot}5 \times 10^{-6}$ for $\parallel$ axis and $13{\cdot}7 \times 10^{-6}$ for $\perp$ axis. Diamond belonging to the cubic system has a cubical coefficient given by

$$\gamma = 3\lambda = {\cdot}00000354 + {\cdot}0000000432\ (\theta - 40)$$

which gives the coefficient of linear expansion as $1{\cdot}2 \times 10^{-6}$. Iceland spar, which is uniaxial, shows expansion parallel to the axis and contraction perpendicular to it ; but the contraction is much less than the expansion and hence the cubical coefficient is positive. Emerald (uniaxial) has the following coefficients :—

$$\lambda_1 = -\ {\cdot}00000106 + {\cdot}0000000114\ (\theta - 40)$$

$$\lambda_2 = +\ {\cdot}00000137 + {\cdot}0000000133\ (\theta - 40)$$

$$\therefore \qquad \gamma = \lambda_1 + 2\lambda_2 = {\cdot}00000168 + {\cdot}000000038\ (\theta - 40\ )$$

The first principal coefficient (λ_1) is negative up to 133°C. It appears, however, that the cubical dilatation is positive above $-4{\cdot}2$°C and negative below it and consequently at this temperature $dv/d\theta = 0$ and the density is maximum.

Practical applications. The expansion of solids is utilised in several ways, in some as a welcome aid while in others as an adverse effect to be overcome. Some of the important applications where it serves a *useful purpose* are :—(*i*) *Metallic thermostat.* It consists of a bimetallic strip made by welding together brass and invar steel. The strip is wound into a small spring and is connected by means of a rod to the contact maker of the circuit of an electric heater. As the temperature rises, the expansion of brass causes the spring to unwind and thereby breaking the contact of the electric circuit. When the temperature falls the spring contracts which permits the contact to be made. With such a device temperatures upto 300°C can be maintained steady within ± 1°C for a long period of time.

(*ii*) *Sealing wire in glass.* Since platinum expands to practically the same amount as glass (chiefly lead glass), platinum wires can be sealed into glass without any risk of a crack developing, which would however happen if other metallic wires such as copper or iron are used, on account of these metals expanding and contracting much more than glass. It may be mentioned in this connection that Guillaume has made a valuable discovery that an alloy of steel and nickel (55% + 45%) has the same coefficient of expansion as glass and hence could be used instead of the more costly platinum.

(*iii*) *Prevention of bulging walls from collapsing.* Walls of buildings which tend to bulge outwards can be drawn together and thereby prevented from collapsing by passing iron rods through them across the building and fixing tightly the extremities of the rods by bolts and nuts to iron plates screwed to the wall on the outside, while the rods are being heated in the centre. When the rods cool, and contract, the walls are pulled together and assume their proper positions.

(*iv*) *Riveting of boiler plates.* Boiler plates are joined with red-hot rivets, which, on cooling draw the plates close together, thereby forming steam-proof joints.

(*v*) *Fitting of metal tyres on cart wheels.* The iron tyres of village cart wheels are fixed in position by heating them until their inner diameters are large enough to get over the wooden rims of the wheels. On cooling they contract and bind the wheels firmly.

Of the ways in which expansion of solids becomes an *obstacle to be removed*, the following are worthy of note :—

(*i*) *Compensated pendulums and balance wheels.* The *time* kept by a *clock* depends upon the time of oscillation of its pendulum, which, in turn, is governed by the length of the pendulum, varying directly as the square root of the length. Hence if the length of the pendulum is increased due to rise in temperature, the time of oscillation increases and the clock loses. If the length decreases due to fall in temperature, the pendulum swings faster, the time of oscillation becomes less and the clock gains. Thus a clock will lose time in summer and gain in winter, unless the pendulum is a compensated one against the effect of expansion. The following types of compensated pendulum have been used with a certain measure of success :—

(*a*) *Wooden pendulum.* The rod of the pendulum is made of wood, while the bob is of metal and of small size. The small expansion of the wooden rod downwards is compensated by that of the bob upwards ; although the metal expands more than wood, yet on account of the small size of the bob, the effective expansion is small and equal to that of the wooden rod.

(*b*) *Grid-iron pendulum* consists of alternate rods of steel and brass connected as shown in Fig. 26, so that the steel rods expand only downwards, while the brass rods only upwards. In order to keep the effective length of the pendulum constant under all conditions of temperature $l_1\alpha_1 = l_2\alpha_2$, where l_1 and l_2 are the total lengths of the steel and brass rods respectively and α_1 and α_2 are the coefficients of linear expansion of the two metals. From the known values of α_1 and α_2, it can be shown that the total length of the steel rods must be about one and half times that of the brass rods.

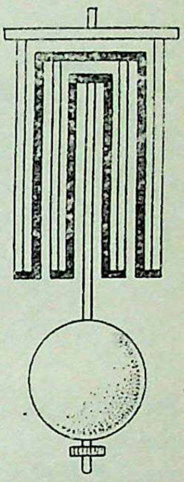


Fig. 26. Grid-iron pendulum.

(*c*) *Mercury pendulum.* In this device a long steel rod carries, in the place of the ordinary bob, a frame fitted with two glass cylinders containing mercury, as shown in Fig. 27. Compensation is obtained due to the fact that, as the rod expands downwards, the mercury expands upwards by an equal amount, provided the quantity of mercury is properly adjusted. From the known values of the coefficients of linear expansion of steel, and of cubical expansion of mercury and of the dimensions of the glass cylinders, the height to which mercury must stand in the cylinders for exact compensation, *i.e.*, to maintain the distance between the top of the rod and the centre of mass of mercury constant at all temperatures, can be estimated.

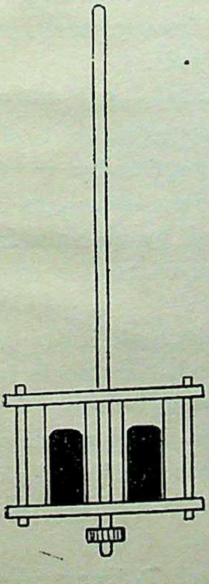


Fig. 27. Mercury pendulum.

In *watches* and *timepieces*, *balance wheels*, oscillating under the influence of steel hair-springs, regulate the rate. The time of oscillation of the balance wheel depends upon the moment of inertia of the wheel about its axis of oscillation. The chief contribution to the moment of inertia comes from small weights W screwed on the rim of the wheel as shown in Fig. 28. A rise of temperature causes the spokes of the wheel to expand pushing the rim and the screw-weights away from the axis. This means an increase in the moment of inertia and the consequent increase in the period of oscillation which causes the watch to lose. To effect compensation, the weights must always be kept at a constant distance from the axis. To secure this condition, the rim of the wheel is made of two metals of different coefficients of expansions, such as brass and steel. The one with smaller coefficient (steel) occupies the inner portion of the rim, while the other with larger coefficient (brass) the outer. This double rim is cut into three sections, and each section supported by a spoke of the wheel carries the screw-weight. The effect of rise of temperature on such an arrangement is that while the inner part of the end of the segment is pushed away from the axis by the expansion of the spoke, the outer part curls towards the axis owing to the greater expansion of the metal there, so that the weights remain at a constant distance from the pivot, in spite of the increase of temperature. Exact compensation is obtained by adjusting carefully the screw-weights on the three sections of the wheel. Only precision watches such as chronometers and wristlets are provided with compensated balance wheels.

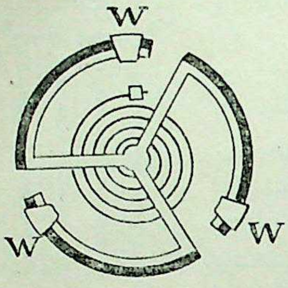


Fig. 28. Balance wheel.

With the introduction of *invar steel* in the manufacture of pendulums and balance wheels the problem of compensation has been eliminated to a great extent, on account of the exceptionally small coefficient of expansion of that alloy. Since, however, invar has a rather high magnetic susceptibility and is affected by changes in earth's magnetic fields, other alloys, such as *elinvar*, of smaller susceptibility, have been produced and utilised.

(*ii*) *Barometric scale*. It is made of steel and the scale is drawn at a particular temperature (usually at 0°C). If the barometer is to be read at any other temperature (above 0°C) the height indicated by the scale will be too small, since the length between the graduation marks is now greater. Using the coefficient of linear expansion of the material of the scale, the correction to be made can be readily calculated.

(*iii*) *A few more interesting examples*. When Railway lines are laid, small gaps must be left between adjacent rails in order to prevent the line from buckling and even breaking due to changes of temperature. (*b*) The end bars of a steel bridge are not firmly built into the pillars of brick on which they rest, but are supported on rollers which allow them to expand or contract without affecting the pillars. (*c*) The moving parts of machinery, such as axles and shafts, are guarded against their expansion due to the heat produced by the use of lubricating oils.

EXPANSION OF LIQUIDS

Study of the thermal expansion of liquids involves problems that are not met with solids. In the first place, since liquids have no definite shape of their own, we have to consider only their volume expansion. Secondly, their coefficients of cubical expansion are ordinarily several hundred times greater than those of solids. Thirdly, while solids expand almost regularly in any temperature range, liquids expand at different rates in different ranges of temperature. Some liquids, such as water, even *contract* at a particular region of temperature. On this account it is usual to distinguish two coefficients of expansion for liquids, *viz., mean and zero coefficients.* The former (γ_m) is defined as the mean increase in volume per unit volume of a liquid per degree rise between any two temperatures and is represented by

$$\gamma_m = \frac{V' - V}{V(\theta' - \theta)} \quad \ldots(1)$$

where V is the volume at any temperature θ and V′ the volume of the same mass of the liquid at a higher temperature θ'.

The latter (γ_0) is defined as the increase in volume per unit volume when a mass of the liquid at 0°C is raised to 1°C, and is represented by

$$\gamma_0 = \frac{V_1 - V_0}{V_0} \quad \ldots(2)$$

where V_0 is the volume at 0°C and V_1 the volume at 1°C.

In either case, if the range of temperature is made very small, we get the *true coefficient* which is represented by

$$\gamma = \frac{dv}{v.d\theta} \quad \ldots(3)$$

where dv is the increase in volume of a liquid of volume v when its temperature is raised by a small amount $d\theta$.

5

From relation (3), we get

$$\frac{dv}{v} = \gamma \,.\, d\vartheta$$

or

$$v = v_0 e^{\gamma\theta} \qquad \ldots(4)$$

Relation (1) can be expressed as

$$V' = V\{1 + \gamma_m(\theta' - \theta)\} \qquad \ldots(5)$$

If the initial volume refers to 0°C, as is often done in precision measurements, then we may write

$$V = V_0\,(1 + \gamma_m\theta) \qquad \ldots(6)$$

where V_0 is the volume at 0°C and V the volume at any higher temperature θ°C.

In dealing with the expansion of liquids it is more convenient to deal with density than volume. Supposing M to be the mass of the volumes of liquid considered above, then its initial and final densities, ρ_0 and ρ, are given by

$$\rho_0 = \frac{M}{V_0}, \quad \rho = \frac{M}{V}$$

Hence equation (6) can be written as

$$\frac{M}{\rho} = \frac{M}{\rho_0}(1 + \gamma_m\theta)$$

$$\therefore \qquad \rho_0 = \rho\,(1 + \gamma_m\theta) \qquad \ldots(7)$$

This is a very useful relation connecting coefficient of expansion of a liquid and its variation of density with temperature, which will be used in the experimental determination of the coefficient of expansion of liquids :—

$$\gamma_m = \frac{\rho_0 - \rho}{\rho\theta} \qquad \ldots(8)$$

If the densities are measured at any other range, say θ_1°C and θ_2°C, then

$$\gamma_m = \frac{\rho_1 - \rho_2}{\rho_2\,(\theta_2 - \theta_1)} \qquad \ldots(9)$$

as already shown in the case of solids (*Cf.* p. 44).

Apparent and absolute expansions. Another important problem encountered with liquids is that they require a *container* to hold them. This means that the cubical expansion of a liquid can, in general, be obtained only relative to the container, which also expands, so that the apparent increase in volume of the liquid will be less than the true increase. Hence it becomes necessary to distinguish two mean coefficients of expansion for liquids :—

The *coefficient of apparent expansion* which is defined as the ratio of the apparent increase in volume of the liquid (relative to the container), per degree rise of temperature, to the original volume of the liquid.

The *coefficient of absolute expansion* which is defined as the ratio of the true increase in volume of the liquid alone, per degree rise of temperature, to the original volume of the liquid.

In practice, it is possible to correct for the expansion of the container and get the absolute expansion, since it can be shown that *the coefficient of absolute expansion of the liquid is approximately equal to the sum of the coefficient of apparent expansion of the liquid and the coefficient of volume expansion of the containing vessel* :—

Let V_0 be the real volume of the liquid at 0°C, V the real volume at θ°C and V_a the apparent volume at θ°C. Let l and m be the apparent and absolute coefficients of expansion of the liquid and g the coefficient of cubical expansion of the container. Then

$$V_a = V_0(1 + l\theta) \qquad \ldots (1)$$

$$V = V_0(1 + m\theta) \qquad \ldots (2)$$

But
$$V = V_a(1 + g\theta) \qquad \ldots (3)$$

considering the expansion of the container.

From (2) and (3),

$$\begin{aligned} V_0(1 + m\theta) &= V_a(1 + g\theta) \\ &= V_0(1 + l\theta)(1 + g\theta), \text{ using (1).} \end{aligned}$$

Or
$$\begin{aligned} (1 + m\theta) &= (1 + l\theta)(l + g\theta) \\ &= 1 + (l + g)\theta \text{ approximately.} \end{aligned}$$

$$\therefore \quad m = l + g \qquad \ldots (4)$$

In the derivation and use of the above relation it is supposed that a hollow container expands just as though it were a solid of the same volume and shape, so that g can be determined by measuring the coefficient of linear expansion of the material of the container in the form of a rod. This assumption is legitimate, since it can be established as follows :—

Considering a rectangular vessel, let L_0, B_0 and D_0 be its length, breadth and depth at 0°C. When it is raised in temperature through θ°C, the above dimensions will become $L_0(1 + \alpha\theta)$, $B_0(1 + \alpha\theta)$ and $D_0(1 + \alpha\theta)$ where α is the coefficient of linear expansion of the walls. If V_0 and V are the initial and final volumes of the vessel,

$$V_0 = L_0 \times B_0 \times D_0$$

and
$$\begin{aligned} V &= L_0(1 + \alpha\theta) \times B_0(1 + \alpha\theta) \times D_0(1 + \alpha\theta) \\ &= L_0 \times B_0 \times D_0(1 + 3\alpha\theta) \\ &= V_0(1 + 3\alpha\theta) \end{aligned}$$

neglecting $\alpha^2\theta^2$ and $\alpha^3\theta^3$, since they are extremely small.

But $3\alpha = g$, where g is the coefficient of cubical expansion of the walls of the vessel.

$$\therefore \qquad V = V_0(1 + g\theta)$$

Thus the vessel expands as if it were a solid of the same shape and volume.

But it can be still objected, since the physical properties of the material may change when it is worked into a container of some shape, chiefly in the case of glass. This difficulty has been overcome to a great extent by using fused silica or quartz containers which have a very insignificant coefficient of cubical expansion, so that the apparent coefficient of a liquid contained in them is almost the same as the absolute coefficient.

Experimental determination of the coefficient of cubical expansion of liquids. In the early researches on expansion of liquids attention was chiefly directed on overcoming the difficulty of the container stated above. This meant devising a way of finding the coefficient of expansion of a liquid which did not involve the expansion of any container. The best means was to compare the densities of the liquid at different temperatures by a method which was unaffected by any change in size of the containing vessel. The method of balancing columns readily suggested itself. Hence different workers undertook the determination of the coefficient of absolute expansion of mercury using the balancing columns method. A series of classical experiments were performed with successive modifications of the technique in order to obtain great accuracy of results. When once the coefficient of absolute expansion of mercury had been thus determined, the problem resolved itself easily. Measuring the apparent expansion of mercury in a given container, the coefficient of cubical expansion of the material of the container was readily obtained Then determinations of the real expansion of any liquid placed in a container of that material could be effectively made and the coefficient of absolute expansion of the liquid could be easily obtained by adding to the coefficient of apparent expansion the known coefficient of cubical expansion of the container. Hence, nowadays, experimental determination of the coefficient of expansion of liquids consists mainly in the measurement of the coefficient of apparent expansion alone. We shall first describe the historical experiments conducted for determining the coefficient of absolute expansion of mercury and then pass on to the modern laboratory methods of determining the coefficient of expansion of liquids in general which directly measure only the coefficient of apparent expansion.

Method of balancing columns for the absolute expansion of mercury. The basic *principle* used in this method is the same as that of determining the relative densities of liquids by balancing columns. The hydrostatic pressure of a column of a liquid depends on the vertical height of the column, the density of the liquid and the acceleration due to gravity, while it is independent of the area of cross-section of the container since pressure is force per unit area. Hence if h_1 and h_2 be the heights of the columns of two liquids of densities ρ_1 and ρ_2 that balance against each other, then

$$h_1\rho_1 g = h_2\rho_2 g \quad \text{or} \quad \rho_1/\rho_2 = h_2/h_1$$

In a similar manner, by balancing two columns of a liquid, one hot and the other cold, the densities of the liquid at the two temperatures can be compared and the absolute coefficient of the liquid can be directly found, since the ratio of the heights of the balancing columns is independent of the dimensions of the container.

Dulong and *Petit* were the first to use this method with a simple U-tube arrangement, shown in Fig. 29. A pretty large U-tube with the limbs A and B wide at their top open ends and the cross-tube CD straight and narrow was used. It was filled with mercury up to a certain height in the wide portions of the limbs. One limb (A) was kept in a bath of melting ice, while the other (B) in an oil bath. The cross-tube CD was arranged to be perfectly horizontal. It was made as narrow as possible in order to minimise the disturbing effect of convection current caused by the difference in temperature of the liquid in the two limbs. The

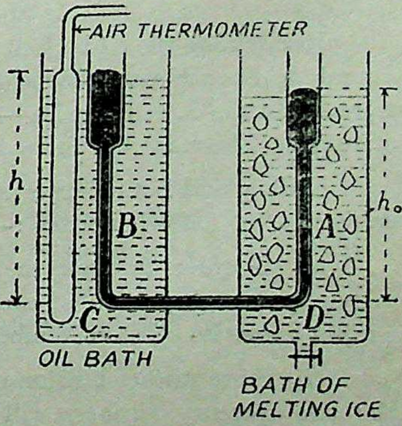


Fig. 29. Apparatus of Dulong and Petit.

wide upper ends of the limbs were meant to reduce the surface tension effect on the mercury surfaces to a minimum. The oil bath was heated by a furnace built round it and its temperature was measured by an air thermometer with a long bulb in order to obtain the mean temperature of the bath. Maintaining the oil bath at any desired constant temperature θ, the levels of the mercury in the two limbs were allowed to become steady. Then the heights h and h_0 of the mercury levels in the hot and cold limbs above the axis of the cross-tube where the disturbance due to convection current would be least, were measured with a cathetometer. Just before measuring these heights, a little cold mercury at 0°C was added to the cold limb if necessary, in order to make the levels to be visible above the baths. Using the values of h_0 and h and 0°C and θ°C thus known, the coefficient of absolute expansion of mercury was calculated as follows :—

From the principle of balancing columns

$$\frac{h}{h_0} = \frac{\rho_0}{\rho}$$

where ρ_0 and ρ are the densities at 0°C and θ°C respectively,

But $$\frac{\rho_0}{\rho} = 1 + m\theta$$

where m is the coefficient of absolute expansion.

$$\therefore \qquad \frac{h}{h_0} = 1 + m\theta$$

Or $$m = \frac{h - h_0}{h_0\theta}$$

Maintaining the oil bath at 100, 200 and 300°C and measuring h and h_0 in each case, the mean coefficient of absolute expansion of mercury for the three ranges 0 — 100, 0 — 200 and 0 — 300°C were obtained. The value was found to increase slightly for higher ranges.

Dulong and Petit's experiment, though simple in design, was subject to the following errors :—

(*i*) In order to read the heights of the mercury levels conveniently a small portion of each of the mercury columns has to project above its constant temperature bath.

(*ii*) Since surface tension varies with temperature its effect on the two mercury surfaces will be different, although this source of error is eliminated to a great extent by making the upper ends of the limbs wide.

(*iii*) The temperature of the hot mercury column cannot be measured accurately in spite of using an air thermometer with a long bulb, since efficient stirring of the oil cannot be easily done.

(*iv*) Since the two limbs are at a large distance apart, the small difference in height ($h - h_0$) of the two columns cannot be accurately measured.

Regnault, in order to avoid these errors, devised two methods. In the first one, two wide and vertical tubes A and B made of iron were connected at their tops by a narrow and horizontal cross-tube CD. The lower ends of A and B were joined by another narrow glass tube EFGHIJ in the form shown in Fig. 30. This tube was in communication with a compression pump through a side tube T. A small hole P was made at the middle of CD in order to keep the top of the liquid at atmospheric pressure. The arrangement was filled with mercury, which was however prevented from rising too far in the limbs FG and IH by working the pump. The tube A was completely enclosed in an oil bath, whereas the other tube B and the portion FGHI were kept in baths of melting ice, hence maintained at 0°C. Keeping the oil-bath at any given constant high temperature θ°C, there would be a steady difference of levels of mercury in FG and IH. The pressure of air over FG and IH were the same, though different from the atmoshperic pressure, while mercury in the tubes A and B exposed to atmospheric pressure would stand at the same level. With such an arrangement the main mercury columns in A and B whose densities were to be compared were completely enclosed by their respective constant temperature baths. The balancing columns were kept at the same temperature, thereby eliminating the surface tension variations on the two mercury surfaces ; besides the limbs being close together, the difference in levels in them could be more easily and correctly measured.

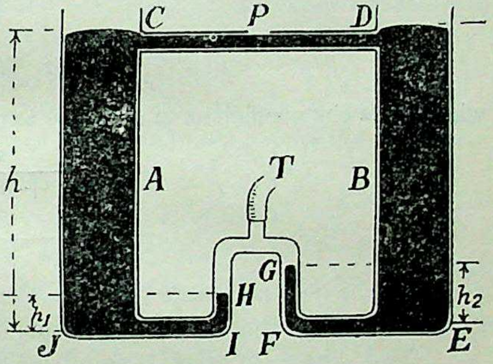


Fig. 30. Regnault's first apparatus.

For determining the coefficient of absolute expansion of mercury the vertical height h of mercury in A or B, the heights h_1 and h_2 in IH and FG were carefully measured.

Considering the limb CAIH, $p - P = hg\rho - h_1 g\rho_0$ where p is the pressure of the air inside the portion FGHI, P the atmospheric pressure, ρ the density of mercury at θ°C and ρ_0 the density at 0°C.

Similarly, for the limb DBFG

$$p - P = hg\rho_0 - h_2 g\rho_0$$

Hence $$hg\rho - h_1 g\rho_0 = hg\rho_0 - h_2 g\rho_0$$

or $$\frac{\rho}{\rho_0} = \frac{h + h_1 - h_2}{h}$$

But $$\frac{\rho_0}{\rho} = 1 + m\theta$$

where m is the coefficient of absolute expansion.

$$\therefore \quad 1 + m\theta = \frac{h}{h + h_1 - h_2}$$

Or $$m = \frac{h_2 - h_1}{(h + h_1 - h_2)\theta}$$

In the second method, with the intention of securing still greater accuracy Regnault modified his apparatus as follows :—

Two pieces of glass tubing BAEG and DCFH were joined at their lower ends by a flexible iron tube BD in order to allow them to expand independently. The two vertical arms AB and CD were about a metre and half long each, the former enclosed in an oil bath and the latter in a bath of melting ice. The portions AE and CF were kept perfectly horizontal. The limbs EG and FH of about 1 cm. in bore were arranged close to each other and enclosed in a bath of melting ice (Fig 31). The whole apparatus was filled with mercury up to a certain height in the limbs EG and FH. When the oil

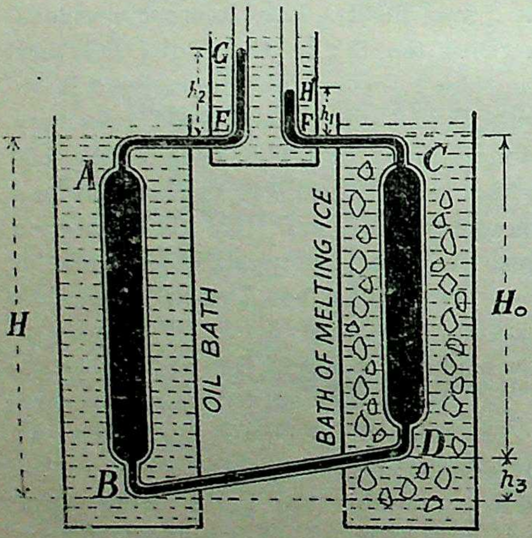


Fig. 31. Regnault's second apparatus.

bath was heated, the density of mercury in AB would be lowered and in consequence the level of mercury in the limb EG would rise while the level in FH would fall. Maintaining the oil bath at any desired constant temperature and allowing the system to reach a steady state the various heights, indicated in the figure, *viz.*, the heights h_1 and h_2 in the limbs FH and EG above the axis of the horizontal portion AEFC, the vertical heights H_0 and H of CD and AB and the vertical height h_3 between B and D, were carefully measured.

The coefficient of absolute expansion of mercury was calculated as follows :—

Since the pressure at G and H are equal, the pressure difference between G and B must be equal to that between H and D. Hence

$$h_2 g \rho_0 + H g \rho = h_1 g \rho_0 + H_0 g \rho_0 + h_3 g \rho'$$

where ρ_0 is the density of mercury at 0°C, ρ the density at the temperature θ of the oil-bath, ρ' the density of mercury in the flexible iron tube which is at the room temperature θ'.

Since $$\rho_0 = \rho(1 + m\theta) = \rho'(1 + m\theta')$$

$$\rho = \rho_0/(1 + m\theta) \text{ and } \rho' = \rho_0/(1 + m\theta')$$

Substituting these values of ρ and ρ', we get

$$h_2 + \frac{H}{1 + m\theta} = h_1 + H_0 + \frac{h_3}{1 + m\theta'}$$

In this equation, all the quantities except m are known. Hence m can be calculated. Although there is a little uncertainty about θ' which is assumed to be at the room temperature, the term involving θ' is so small that slight discrepancy in the value of θ' cannot vitiate the accuracy of results.

With this improved and simpler form of apparatus, Regnault made a very large series of measurements between temperatures of 0°C and 350°C. Plotting his data on a curve, he estimated the values of the mean coefficient of absolute expansion of mercury at different ranges from the curve and obtained the following results :

m = ·001815 for the range 0°—100°C
m = ·001841 for the range 0°—200°C
m = ·001866 for the range 0°—300°C

Callendar and *Moss*, with the intention of getting results with a still higher degree of accuracy, introduced an ingenious modification based on the fact that the longer the two columns that were balanced against each other the greater would be the accuracy in the measurements. While Regnault had used a single pair of hot and cold columns $1\frac{1}{2}$ metres long, they employed six such pairs each 2 metres long connected in series, as shown in Fig. 32. The tubes were made of steel with the horizontal portions of very narrow bore of about 1 mm. The alternate tubes H and C were hot and cold. By suitably bending the horizontal connections between the tubes, all the hot tubes were arranged, one behind the other closely so that they could be conveniently enclosed in a single bath ; similarly all the cold tubes put close together could be introduced in another bath. Electrically heated oil was made to circulate in the bath containing the hot tubes while the bath containing the cold tubes was filled with melting ice. Motor driven stirrers were used in both the baths. Platinum thermometers with long resistane elements were used to measure the mean temperatures of the baths. The apparatus was filled with mercury until it reaches a decent height in the first and last columns. With such an arrangement the effective difference in heights of the mercury level in the first and the last columns would be six times that due to a single pair. Further, since the lengths of the tubes were greater than those in Regnault's apparatus they found that the difference in level was about eight times that observed in Regnault's arrangement. Conducting experiments in the range 0 to 300°C, they were able to claim an accuracy of 1 in 10,000. They got a value of 0·000182 sensibly constant for the absolute expansion of mercury in the range 0 to 100°C, slightly higher than that obtained by Regnault. The values for other ranges were also systematically different from those of Regnault and earlier workers.

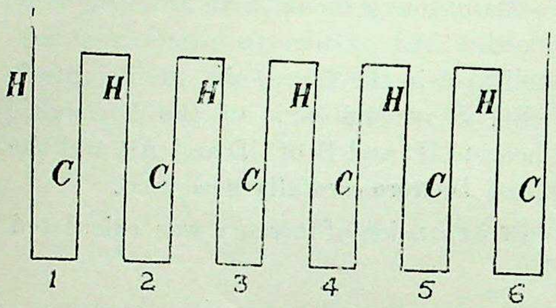


Fig. 32. Apparatus of Callandar and Moss

Although the methods of balancing columns described above can be used for *any* liquid, it is not usually done on account of the elaborate design of apparatus and the many precautions to be taken against several sources of error. Hence in practice the coefficients of absolute expansion of liquids are estimated in the following ways :—

Employing a fused silica or quartz vessel as container of the liquid. As already indicated, due to the very small coefficient of expansion of the material of such a container (0·0000015) the discrepancy between the two coefficients, apparent and absolute, will be of the order of 1 in 1,000, which result is accurate enough for all practical purposes. *Using containers of other materials.* Their coefficients of cubical expansion (g) are determined by independent experiments with mercury, whose coefficient of absolute expansion is accurately known. The absolute expansion of the liquid is then given by the sum of its coefficient of apparent expansion and the coefficient of cubical expansion of the container ($m = l + g$). Sometimes the expansion of the container is compensated by introducing into the container a certain amount of mercury whose expansion is just equal to that of the container used. In such a case the coefficient of expansion experimentally determined will give directly the coefficient of absolute expansion.

Determination of the coefficient of apparent expansion. There are three commonly used methods for finding the coefficient of apparent expansion of liquids :—

(1) the volume thermometer, (2) the weight thermometer and (3) the hydrostatic methods.

The volume thermometer or dilatometer. It consists of a bulb blown at one end of a piece of thermometer tubing. (Fig. 33). The volume of the bulb and the volume of each division of the stem are first determined. The bulb and part of the stem are then filled with the liquid and the volume V_0 of the liquid at 0°C found. The dilatometer is next placed in a bath and its temperature raised. The temperatures at which the liquid column rises to the various graduations in the stem can be found. For a given rise in temperature t°C, if the increase in volume is v which can be readily calculated from the known volume corresponding to each division, the coefficient of apparent expansion is given by :—

$$\gamma = \frac{v}{V_0 t}$$

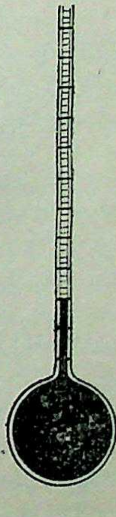


Fig. 33. Volume dilatometer.

If the initial temperature is not 0°C but t_1°C and the final temperature t_2°C, then

$$\gamma = \frac{V_2 - V_1}{V_1(t_2 - t_1)} = \frac{\text{increase in volume}}{\text{original volume} \times \text{change of temperature}}$$

The weight thermometer. This offers a more accurate method, since it is based on the determination of weight and not of volume. The basic *principle* involved is the comparison of densities at two different temperatures of the liquid whose coefficient of apparent expansion is to be determined. Hence the *specific gravity bottle* readily lends itself as a simple means for doing this. But two other better forms of apparatus are ordinarily used :—

The weight thermometer, which consists of a glass bulb with one end drawn out into a capillary tube as shown in Fig. 34. It is first weighed and then filled with the liquid whose coefficient of apparent expansion is to be determined. Filling the weight thermometer without any air bubble is somewhat difficult. The bulb is warmed to expel some air from inside it and the nozzle is dipped in a beaker containing the liquid, some of which is drawn in when the bulb cools. The bulb is then heated until the liquid boils and vaporises so that the vapour may drive out all the air. The nozzle is again immersed in the liquid, when the thermometer will be completely filled as the bulb cools causing the vapour to condense. It is necessary to use liquid which has been previously boiled to make it air-free. Even then a small air-bubble often appears at the neck, which must be got rid of by gently heating the bulb and immersing the nozzle in the liquid. After thus having filled the thermometer, it is immersed in a cold water bath for some time in order that it may acquire the temperature of the bath, which is noted. The thermometer is taken out, dried on the outside and weighed. It is again immersed in a water bath and the bath heated. As the temperature rises, the liquid expands and oozes out through the nozzle. Maintaining the bath at any desired temperature, all overflow of liquid from the nozzle is gently removed with a blotting paper. When the liquid has stopped expanding, the thermometer is taken out, its outside wiped well and after cooling weighed again. From the three weighings thus made the coefficient of apparent expansion can be estimated as will be indicated below.

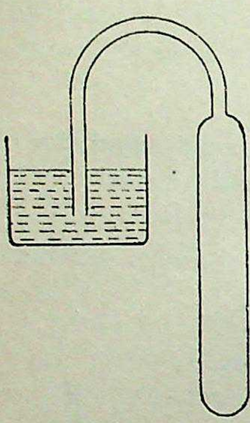


Fig. 34. Weight thermometer.

Another design of the weight thermometer which can be more easily filled with the liquid is known as the *pyknometer*. It is a U-shaped glass tube of fine bore with a cylindrical bulb as part of one arm (Fig. 35). The free ends of the arms are bent at right angles, away from each other and along the same line. The end close to the bulb is drawn out into a nozzle while the other end remote from the bulb has a mark on it to indicate the level to which the pyknometer is to be filled. To fill the pyknometer with the liquid without any bubble, a piece of India rubber tubing is attached to the end with the mark, the pyknometer is inverted with the nozzle dipping in the liquid as shown in the figure. By sucking out air through the rubber tube the liquid is drawn in. To avoid air bubbles getting lodged in the bends, the bulb should be kept as far as possible vertical, particularly when the level of the liquid has gone almost to the top of the bulb. The rest of the experiment is carried out exactly as in the case of the weight thermometer, taking care, however, that the liquid level is always maintained constant against the mark.

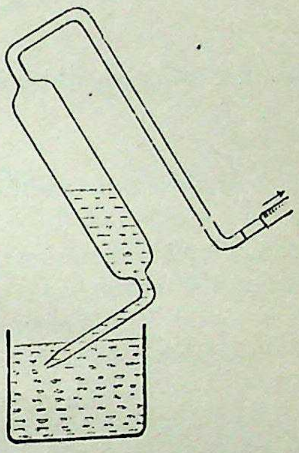


Fig. 35. Pyknometer.

Whatever be the form of the container used, whether a specific gravity bottle or a weight thermometer or a pyknometer, the coefficient of apparent expansion is calculated from the three weighings made and the two temperatures noted as follows :—

Weight of the apparatus empty...... $= w$ gms.

Weight of the apparatus + liquid filling it initially at t_1°C...... $= w_1$ gms.

Weight of the apparatus + liquid filling it finally at t_2°C...... $= w_2$ gms.

Weight of the liquid that fills the apparatus at t_1°C...... $= w_1 - w = m_1$ gms.

Weight of the liquid that fills the apparatus at t_2°C...... $= w_2 - w = m_2$ gms.

Since m_1 and m_2 are the weights of the liquid *filling the same volume* V of the apparatus, at temperatures t_1 and t_2, if ρ_1 and ρ_2 are the corresponding densities, we may write

$$V = \frac{m_1}{\rho_1} = \frac{m_2}{\rho_2} \text{ or } \frac{m_1}{m_2} = \frac{\rho_1}{\rho_2}$$

But
$$\frac{\rho_1}{\rho_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1}$$

where γ is the coefficient of apparent expansion.

$$\therefore \qquad \frac{m_1}{m_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1}$$

$$\text{Or} \qquad \frac{m_1 - m_2}{m_2} = \frac{\gamma(t_2 - t_1)}{1 + \gamma t_1}$$

$$= \gamma(t_2 - t_1) \text{ approximately,}$$

i.e., neglecting γt_1 which is very small compared with 1.

$$\therefore \qquad \gamma = \frac{m_1 - m_2}{m_2\,(t_2 - t_1)}.$$

Hydrostatic method. This was first employed by Matthiessen in his researches on the expansion of water ; but it can be utilised for any liquid. The *principle* involved is that of *Archimedes*, ordinarily used in the measurement of density, *viz.*, when a body is immersed in a liquid it suffers an apparent loss of weight equal to the weight of the liquid of the same volume as the body.

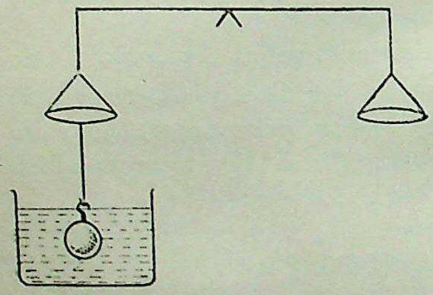


Fig. 36. Hydrostatic method.

A sinker, which may be a glass rod or sphere or even a bulb suitably weighted with lead shots, is first weighed in air using a hydrostatic balance and then immersed in the liquid whose coefficient of apparent expansion is to be determined and weighed again (Fig. 36). The liquid is heated to some suitable temperature and the sinker is weighed once more while the temperature is maintained constant, which is not quite easy in practice. In order to avoid inaccuracy in weighing the liquid is arranged under the balance case and the sinker is suspended from the balance by a fine wire passing through a hole in the bottom of the case. From the three weighings of the sinker made and the initial and final temperatures of the liquid recorded, the coefficient of apparent expansion of the liquid can be calculated as follows :—

The weight of the sinker in air $= w$ gms.
Its weight when immersed in the cold liquid at t_1°C $= w_1$ gms.
Its weight in hot liquid at t_2°C $= w_2$ gms.
The loss of weight in the cold liquid $= w - w_1$ gms. $= m_1$ gms.
The loss of weight in the hot liquid $= w - w_2$ gms. $= m_2$ gms.

If ρ_1 and ρ_2 are the densities of the liquid at t_1°C and t_2°C, by Archimedes' principle,

$$m_1 = V\rho_1 \text{ and } m_2 = V\rho_2$$

where V is the volume of the sinker which is assumed to be constant ignoring its expansion.

$$\therefore \qquad \frac{m_1}{m_2} = \frac{\rho_1}{\rho_2}$$

$$\text{But} \qquad \frac{\rho_1}{\rho_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1}$$

where γ is the coefficient of apparent expansion.

$$\frac{m_1}{m_2} = \frac{1 + \gamma t_2}{1 + \gamma t_1}$$

This leads, as in the case of the weight thermometer, to

$$\therefore \qquad \gamma = \frac{m_1 - m_2}{m_2(t_3 - t_1)}$$

Results. Accurate measurements, as in the case of mercury, show that no liquid expands uniformly and that the mean coefficient of absolute expansion m increases with temperature. Taking, therefore, m to be the from $m = a + b\theta$,

$$V = V_0(1 + m\theta) = V_0(1 + a\theta + b\theta^2)$$

$$\text{If} \qquad V_0 = 1, \; V = 1 + a\theta + b\theta^2.$$

The *true* coefficient of absolute expansion m_θ is given by

$$\frac{1}{V} \cdot \frac{dV}{d\theta} = \frac{1}{1 + a\theta + b\theta^2} \cdot \frac{dV}{d\theta} = \frac{a + 2b\theta}{1 + a\theta + b\theta^2}$$

The *zero* coefficient of absolute expansion m_0 is given by

$$\frac{1}{V_0} \cdot \frac{dV}{d\theta} = a + 2b\theta.$$

Expansion of water. The expansion of water is so markedly irregular that even ordinary laboratory methods can detect the anomaly. From 0° to 4°C, water, instead of expanding, actually contracts ; from 4°C upwards it expands, but far from uniformly. In the range 5° to 10°C, the coefficient of expansion is only $0{\cdot}53 \times 10^{-4}$, whereas in the range 20° to 40°C it is $3{\cdot}02 \times 10^{-4}$ and between 60° and 80°C, $5{\cdot}87 \times 10^{-4}$. Hence a given mass of water has its volume a minimum or its density a maximum at 4°C. In other words, in the expression for the coefficient of expansion $\dfrac{dv}{v \,.\, dt}$ is negative for temperatures less than 4°C and positive for temperatures greater than 4°C. At 4°C $dv/dt = 0$.

The expansion of water is of special interest, not only because water is so much used in everyday life, but also because it forms the physical basis of the unit of mass. Hence many workers, such as Hope, Despretz, Haellstrom, Hagen, Matthiessen, Joule, Playfair and others have made careful researches on the anomalous expansion of water. We shall here describe briefly some of the many experiments thus performed.

1. *Constant volume dilatometer* has been used as a simple laboratory method. The dilatometer is effectively made to maintain its volume constant for the range of temperature to be studied by constructing it with fused silica or quartz, whose expansion is negligible or, if made with ordinary glass, by introducing enough mercury into the bulb so that the expansion of mercury just compensates the expansion of the bulb ; in this latter case, since the coefficients of expansion of mercury and glass are ·000182 and ·0000255 respectively, the amount of mercury required for compensation is $\cdot 0000255/\cdot 000182 = \frac{1}{7}$ of the volume of the dilatometer used.

After filling such a constant volume dilatometer with air-free water to a convenient height in the graduated stem, it is placed in a bath of ice and water, provided with an accurate thermometer and a stirrer. When the temperature of the bath is steady at 0°C, the reading of the level of water in the stem is noted. The bath is gently heated until its temperature is 2°C which is maintained steady for some time ; then the water is stirred well and the reading of the level taken. This process is repeated for every 2° up to 10°C and for every 5°C up to 100°C. The readings are checked by allowing the water to cool again to zero, and the mean of the two readings at any given temperature is used.

It is found that as the temperature of the bath is increased from 0°C to 4°C, the level of water in the stem falls first slowly and then very slowly until 4°C is reached, thus indicating that water contracts in this region. From 4°C to 8°C, the level rises again, showing that water expands, until at about 8°C, the level is the same as at 0°C. Thereafter the level rises, at first very slowly and then more rapidly with increase of temperature up to 100°C. Hence at 4°C, the volume is least, or, in other words, water has maximum density at 4°C.

With the readings recorded, the variation in volume of 1 gram of water with temperature can be studied as follows :—

If the volume corresponding to each division of the graduated stem of the dilatometer is known, the decrease or increase in volume at any temperature can be calculated and the volume of 1 gram of water can be estimated at that temperature. Plotting the data thus obtained, *i.e.*, volume of 1 gram of water against temperature the graph is of the form shown in Fig. 37. It is seen that the specific volume decreases first, reaching a minimum value at 4°C and then increases ; it is evident that the density curve will follow an inverse path, increasing from 0° to 4°C, where it reaches a maximum and then decreasing. Its value at 0°C is 0·9998, at 4°C 1·000, at 8°C again 0·9998 and at 100°C 0·9587. It may be noted that the curve is not linear and hence the expansion is not uniform even beyond 4°C.

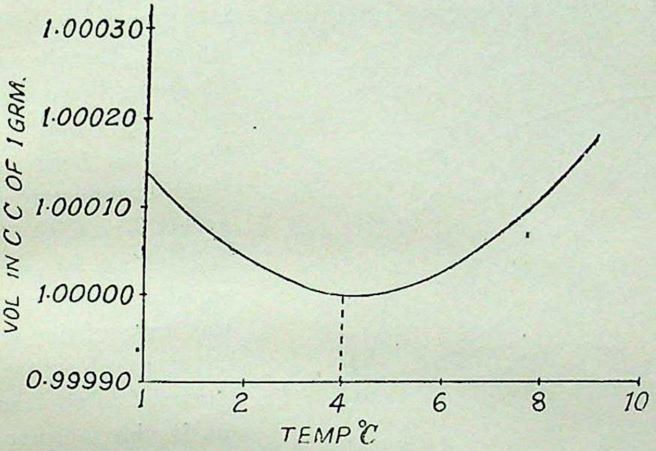


Fig. 7.

2. *Hope's experiment.* Hope devised a simple arrangement, ordinarily known as *Hope's apparatus*, and used for demonstrating the anomalous behaviour of water as regards its expansion. It can be used also to determine the *temperature of maximum density of water* with a fair degree of accuracy, as was done by Despretz.

The apparatus consists of a tall metal cylinder A, provided with two side openings fitted with thermometers C and D near the top and bottom and surrounded at the centre with a circular trough B. (Fig. 38). The cylinder is filled with ordinary cold water, and the outer trough with a freezing mixture of ice and salt. The temperature

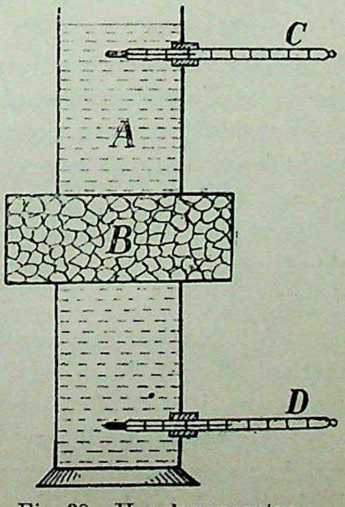


Fig. 38. Hope's apparatus.

of the water at the top and bottom is measured with the two thermometers at regular intervals of time and the temperature-time curves of C and D are drawn, as shown in Fig. 39. The point P at which the two curves cross each other gives the temperature of maximum density. The two curves are interpreted as follows :—

As the freezing mixture cools the layer of water at the centre, the latter contracts, becomes denser and consequently sinks to the bottom, thereby causing the lower thermometer D fall very rapidly, while the upper thermometer C remains almost unchanged except for a slight fall due to cooling by the very small conduction through the water from the cold layer at the centre. This state of affairs continues until the temperature of the central layer falls below 4°C. At this stage expansion sets in, the central layer becomes less dense than the water below it, so that it rises upwards and cools the water above it. Hence the top thermometer C falls, while the lower thermometer D remains stationary at the temperature of maximum density until such time as the water above becomes colder, when heat will slowly be taken from D by conduction. As soon as the water in the region of C becomes more dense than the central layer, the temperature of C falls rapidly to zero and ice begins to form first on the top of the water. The water at the bottom is still at the temperature of about 4°C, which, therefore, indicates, approximately the temperature of maximum density of water.

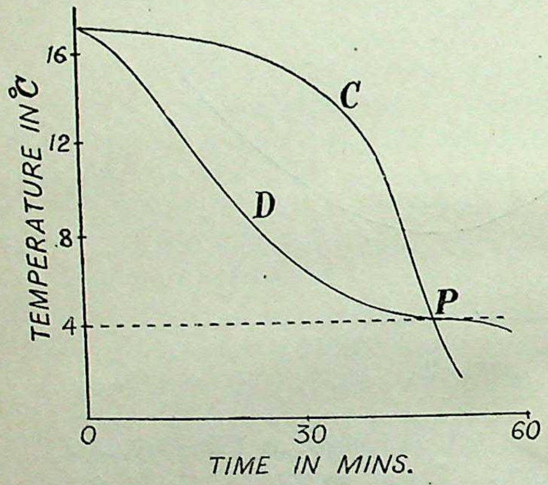


Fig. 39.

3. *Matthiessen's researches.* Matthiessen used the hydrostatic method (already described *Cf*. p. 78) to determine the temperature of maximum density of water as follows :—

A glass sphere is used in a hydrostatic balance and its loss of weight measured when immersed in water at different temperatures. If the loss of weight at 0°C is w_0 and at t°C w_t,

$$w_\theta = w_0(1 + \alpha\theta + \beta\theta^2 + \gamma\theta^3)$$

α, β, γ can be determined from the data obtained for different temperatures :

$$\alpha = 5{\cdot}8815 \times 10^{-5}$$
$$\beta = -6{\cdot}2216 \times 10^{-6}$$
$$\gamma = 1{\cdot}443 \times 10^{-8}$$

If the volume of the sphere at 0°C is v_0 and at θ°C v_θ

$$v_\theta = v_0(1 + a\theta + b\theta^2)^3$$

where a and b are constants determined by measuring the coefficients of linear expansion of a rod made of the material of the sphere at two different temperatures.

If ρ_0 is the density of water at 0°C and ρ at θ°C,

$$\rho = \frac{w_\theta}{v_\theta} = \frac{w_0(1 + \alpha\theta + \beta\theta^2 + \gamma\theta^3)}{v_0(1 + a\theta + b\theta^2)^3}$$
$$= \rho_0(1 + l\theta + m\theta^2 + n\theta^3)$$

where the coefficients, l, m, n are known in terms of α, β, γ and a, b.

The maximum density is given by the condition $\left(\frac{d\rho}{d\theta}\right)_{\theta_0} = 0$, where θ_0 is the temperature of maximum density.

But $$\frac{d\rho}{d\theta} = \rho_0(l + 2m\theta_0 + 3n\theta_0^2)$$

$$\therefore \quad 3n\theta_0^2 + 2m\theta_0 + l = 0$$

$$\theta_0 = \frac{-2m \pm \sqrt{4m^2 - 12nl}}{ln}$$

Substituting the values of $l = 5{\cdot}2939 \times 10^{-5}$, $m = -6{\cdot}5372 \times 10^{-6}$ and $n = 1{\cdot}445 \times 10^{-8}$, θ_0 is found to be equal to 3·989°C.

4. *Joule and Playfair's method.* Joule and Playfair devised an ingenious method to determine as accurately as possible the temperature of maximum density. Their apparatus consists of two tall cylinders A and B connected at the bottom by a tube provided with a tap T and at the top by a trough C which can be closed with a slide (Fig. 40). The cylinders are filled with hot and cold water at temperatures near to and about equidistant from that of the maximum density. The tap is closed and the slide is inserted in the trough ; the water in each cylinder is stirred well and its temperature noted. The cylinders are then put in communication by opening the tap and removing the slide and any flow is detected by placing a glass

bead in the trough and observing its motion. If the direction of motion of the bead shows a flow from the hot to the cold cylinder in the trough and hence from the cold to the hot through the tap, it means that the cold water is more dense than the hot and that its temperature is more distant from that of the maximum density than the temperature of the hot water. In such a case the mean temperature of the hot and cold water is less than that of maximum density, assuming that the density-temperature curve is symmetrical about the temperature of maximum density. If the flow is in the opposite direction, the mean temperature will be greater, and if no flow takes place the mean temperature is equal to the temperature of maximum density.

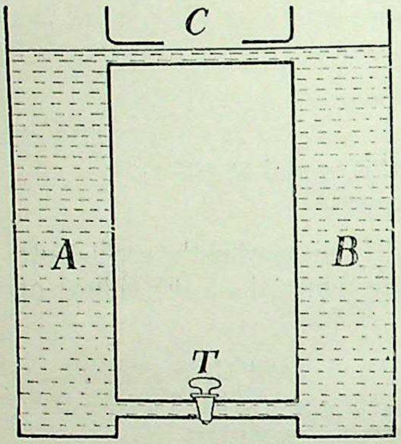


Fig. 40. Apparatus of Joule and Playfair.

In practice, as it is not possible to obtain this ideal condition, the speed of the bead is measured for various mean temperatures and a graph is drawn with the data obtained. The mean temperature corresponding to zero speed, as read from the graph, gives the temperature of maximum density. Joule and playfair obtained thus a value of 3·95°C, which is considered to be the most accurate result so far estimated.

It may be noted that the temperature of maximum density recedes toward 0°C with increase of pressure at the rate of 0·025°C per atmosphere.

A few other substances, such as, iron, bismuth, antimony, expand when they solidify, like water, but most substances contract on solidifying.

Units of mass and volume. In order to have a simple relation between the units of mass and volume, the *gram* was originally defined to be the mass of 1 c.c. of pure water at the temperature of its maximum density. Soon after this was agreed upon, a *standard kilogram of platinum* was made, as the unit of mass and preserved in Paris. This unit was, however, found not to agree with the above definition. The difference, though small, could not be overlooked in very accurate work. The difficulty has been overcome by adopting a new definition of the litre which was formerly either 1000 c.c. or the volume of 1 kilogram of pure water at the temperature of its maximum density. These two quantities are no longer the same. The *litre* is now defined as the volume of 1 kilogram of pure water at the temperature of its maximum density, under one standard atmosphere. On this definition 1 litre = 1000·028 c.c. and the *millilitre* = 1·000028 c.c. which are now widely used as the units of volume, while the units of mass are the standard *kilogram* of platinum and the *gram* which is one-thousandth part of the above standard. The maximum density of water is 1 gram per millilitre and thus the simplicity of the old definition is preserved.

The anomalous behaviour of water has been explained on the assumption that there exist three types of water molecules, H_2O, $(H_2O)_2$ and $(H_2O)_3$ which have different specific volumes and are mixed in different proportions at different temperatures, so that the maximum density at 4°C is probably due to greater proportions of the higher types.

Practical applications. Just as in the case of solids, applications of the expansion of liquids may be classified under two heads, those in which it serves as an aid and those in which it acts as an obstacle to be overcome.

The following examples show how the *expansion of liquids serves a useful purpose.*

(*a*) *Determination of the coefficient of cubical expansion of a solid with a weight thermometer.* Dulong and Petit employed the weight thermometer to find the coefficients of cubical expansion of solids like iron and platinum.

The solid is taken in the form of a small bar which can be conveniently introduced into the bulb of a weight thermometer made of glass, before drawing the capillary part. Before enclosing the bar in the weight thermometer its weight and its density at 0°C are determined. If W_0' and ρ_0' be these quantities, then the volume of the solid at 0°C $= W_0'/\rho_0'$. The empty weight thermometer with the solid alone inside is weighed. Then it is filled with mercury and weighed again. From these two weighings the weight of mercury hat fills the space inside the weight thermometer unoccupied by the solid is obtained. Let W_0 and ρ_0 be the weight and density at 0°C of mercury thus filling the weight thermometer. Heating the weight thermometer in a bath to θ°C, the mercury that overflows is gathered and its weight accurately determined. Let it be w_0. Then the weight of mercury left in the weight thermometer is $(W_0 - w_0)$ and the volume of the mercury at θ°C is $\frac{W_0 - w_0}{\rho_0}(1 + m\theta)$, where m is the absolute coefficient of expansion of mercury. The volume of the solid at $\theta°\text{C} = \frac{W_0'}{\rho_0'}(1 + x\theta)$ where x is the coefficient of cubical expansion of the solid.

The volume of the weight thermometer at 0°C

$$= \frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}$$

The volume of the weight thermometer at θ°C

$$= \left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right)(1 + g\theta)$$

where g is the coefficient of cubical expansion of glass.

Since the volume of the weight thermometer at θ°C is equal to the volumes of mercury left inside and of the solid at the same temperature.

$$\left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right)(1 + g\theta) = \frac{W_0'}{\rho_0'}(1 + x\theta) + \frac{W_0 - w_0}{\rho_0}(1 + m\theta)$$

Or $$\left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right) + \left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right)g\theta = \frac{W_0'}{\rho_0'} + \frac{W_0'}{\rho_0'}x\theta + \frac{W_0}{\rho_0} + \frac{W_0}{\rho_0}m\theta - \frac{w_0}{\rho_0}(1 + m\theta)$$

Or $$\left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right)g\theta = \frac{W_0'}{\rho_0'}x\theta + \frac{W_0}{\rho_0}m\theta - \frac{w_0}{\rho_0}(1 + m\theta)$$

and $$x = \frac{\left(\frac{W_0}{\rho_0} + \frac{W_0'}{\rho_0'}\right)g\theta + \frac{w_0}{\rho_0}(1 + m\theta) - \frac{W_0}{\rho_0}m\theta}{\frac{W_0'}{\rho_0'}\cdot\theta}$$

In this expression, W_0, W_0', w_0, ρ_0, ρ_0' and θ are known ; m and g are taken from the tables. Hence x, the coefficient of cubical expansion of the solid, can be evaluated.

(*b*) *Mercury pendulum*. In this type of compensated pendulum the most important thing is to determine the height up to which mercury should stand in the glass cistern which constitutes the bob. It can now be readily calculated as follows :—

Let l be the length of the steel rod at 0°C and h the height of mercury in the cistern at 0°C. Let v be the volume of that mercury and s the area of cross-section of the cistern at 0°C. Hence $h = v/s$.

If the temperature rises from 0°C to t°C, the length of the rod increases to $l\ (1+\alpha t)$ where α is the coefficient of linear expansion of steel, the area of cross-section of the cistern increases to $s(1 + 2gt)$ where g is the coefficient of linear expansion of glass, and the volume of mercury increases to $v(1 + mt)$, where m is the coefficient of cubical expansion of mercury. The height of the mercury in the cistern therefore increases by

$$\frac{v(1 + mt)}{s(1 + 2gt)} = h\frac{(1 + mt)}{(1 + 2gt)}$$

Since the centre of mass of the mercury is at a height of $h/2$ from the bottom at 0°C, it will rise at t°C to $\frac{h}{2} \cdot \frac{(1 + mt)}{(1 + 2gt)}$ from the bottom.

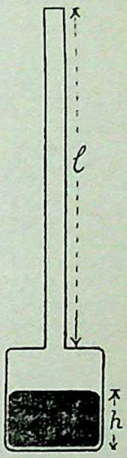


Fig. 41.

For exact compensation, the increase in the length of the rod must be equal to the increase in height of the centre of mass of the mercury.

The increase in the length of the rod $= l(1 + \alpha t) - l = l\ .\ \alpha t.$

The increase in the height of the centre of mass of the mercury

$$= \frac{h}{2}\ \frac{(1 + mt)}{(1 + 2gt)} - \frac{h}{2}$$

$$= \frac{h}{2}(1 + mt)(1 - 2gt) - \frac{h}{2}$$

$$= \frac{h}{2}(1 + mt - 2gt) - \frac{h}{2}$$

$$= \frac{h}{2}(mt - 2gt)$$

$$\therefore \qquad l\ .\ \alpha t = \frac{h}{2}(mt - 2gt)$$

$$\text{Or} \qquad h = \frac{2\alpha}{m - 2g}\ .\ l$$

Substituting the values of $\alpha = 12 \times 10^{-6}$,

$m = 1{\cdot}82 \times 10^{-4}$ and $g = 8{\cdot}5 \times 10^{-6}$,

$$h = \frac{24 \times 10^{-6}}{(182 - 17) \times 10^{-6}} \, . \, l = \frac{24}{165} \, l = \cdot 145 \, l$$

Hence the height of mercury in the cistern should be ·145 times the length of the steel rod.

(*c*) *Toluene thermostat*. It consists of a long bulb T which is filled with a liquid that has a large coefficient of expansion, such as toluene. The liquid is in contact with a mercury column M (Fig. 42). The bulb T is immersed in the bath whose temperature is to be maintained constant. The bath is heated by a burner and the gas supply for it enters through the tube A, proceeds through the tube B as indicated by the arrows. If the temperature of the bath rises sufficiently, the toluene expands and pushes the mercury up until the opening of B is blocked and the gas supply cut off. Actually a small side tube C allows some little gas to pass in order to keep the flame burning, but the heat supplied is not enough to maintain the temperature of T. Hence, the toluene contracts, the opening of B is increased and more gas passes to the burner. By regulating the amount of mercury in the reservoir R, the temperature can be kept constant at any desired value accurate to one or two degrees. If the bath is heated electrically, the moving column of mercury is used to make and break the heating current. The toluene thermostat may be used up to about 100°C, while for higher temperatures the metallic thermostat is to be employed.

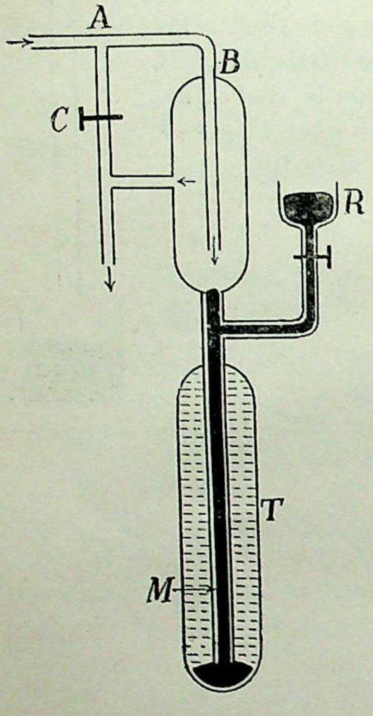


Fig. 42. Toluene thermostat.

(*d*) *Freezing of lakes and ponds in winter*. Nature has made the best use of the anomalous expansion of water. The facts that water has its maximum density at 4°C and that water at 0°C expands when it becomes ice at 0°C have enabled aquatic animals to live on for long periods of time at the bottom of lakes and ponds in spite of the top surface being frozen during winter. Ice remains at the top being less dense than the water below at 4°C. Also, since ice is a poor conductor of heat it does not readily permit heat to be conducted from the water below to the colder air above. If water contracted continuously on cooling and on solidifying, it would freeze from bottom upwards and in very cold weather the whole of a lake would freeze and fishes could no longer live in it.

We shall now give a few examples where *the expansion of liquids becomes a source of error to be corrected.*

(*a*) *Correction of the barometric height for temperature.* The atmospheric pressure is ordinarily expressed in terms of the height of a column of mercury at 0°C which exerts an equivalent pressure. The actually observed reading of a barometer at t°C has to be reduced to the equivalent height at 0°C. To make this correction for temperature, we have to take into account both the expansion of the scale and the change in density of the mercury.

Let H represent the observed height of the barometer at t°C and H_0 the correct height at 0°C. Let l be the coefficient of linear expansion of the material of the scale and m the coefficient of absolute expansion of mercury. Let ρ_0 and ρ be the densities of mercury at 0° and t°C respectively.

Correcting first for the expansion of the scale, the height will be $H(1 + lt)$.

Applying next the correction for the change in density of mercury,

$$H(1 + lt)\rho = H_0\rho_0$$

But $$\rho_0 = \rho(1 + mt)$$

$$\therefore \quad H(1 + lt) = H_0(1 + mt)$$

$$\therefore \quad H_0 = H\frac{1 + lt}{1 + mt} = H(1 + lt)(1 - mt)$$

$$= H\{1 - (m - l)t\}.$$

Supposing a barometer reads 755 mm. on a day when the temperature is 25°C, using the known values of $m = 1{\cdot}82 \times 10^{-4}$ and $l = 12 \times 10^{-6}$, the atmospheric pressure corrected for temperature is

$$H_0 = 755\{1 - (182 - 12) \times 10^{-6} \times 25\}$$

$$= 755\{1 - 170 \times 25 \times 10^{-6}\}$$

$$= 755(1 - {\cdot}00425)$$

$$= 755 - 3{\cdot}21 = 751{\cdot}79 \text{ mm.}$$

(*b*) *Correction for the emergent column of a mercury thermometer.* We have already dealt with this correction in the previous chapter (*Cf.* p. 12). We shall now supplement it with a numerical example :

A mercury thermometer immersed up to 30° mark in a bath reads 230°C. If the average temperature of the emergent column is 50°C, calculate the correct temperature, given the coefficient of absolute expansion of mercury $(m) = 1{\cdot}82 \times 10^{-4}$ and the coefficient of cubical expansion of glass $(g) = 24 \times 10^{-6}$.

The correction for the emergent column (x) is given by

$$\begin{aligned}
x &= \frac{m-g}{(1+mt')(1+gt)} \times (t-t_1)(t-t') \ldots (Cf.\ \text{p. } 13) \\
&= (m-g)(1-mt'-gt)(t-t_1)(t-t') \\
&= 10^{-6}(182-24)\times(1-182\times10^{-6}\times50-24\times10^{-6}\times230) \\
&\qquad \times(230-30)\times(230-50) \\
&= 10^{-6}\times158(1-9{\cdot}1\times10^{-3}-5{\cdot}5\times10^{-3})\times200\times180 \\
&= 10^{-6}\times158\times{\cdot}9854\times200\times180 \\
&= 1{\cdot}58\times9{\cdot}854\times3{\cdot}6\times10^{-1} = 5{\cdot}6
\end{aligned}$$

$\therefore$ The corrected temperature $= 230 + 5{\cdot}6$

$= 235{\cdot}6$°C.

EXPANSION OF GASES

Study of the thermal expansion of gases is, in a sense, much more important than that of solids and liquids, since it has not only provided the most reliable and standard device of measuring temperature, but also led to universal laws governing the behaviour of gases, as already stated in the previous chapter.

When gases are heated they expand much more than liquids, so that the difficulty of the container does not arise seriously and the errors due to the expansion of the container are negligibly small. But we are obliged to consider a new factor with gases, since they are highly compressible and their volume depends not only on temperature but also on pressure.

Coefficients of expansion of a gas at constant pressure and constant volume. Hence, it is necessary to distinguish two coefficients of expansion for gases, *viz.*, *volume coefficient, i.e.*, the coefficient of increase in volume at constant pressure and *pressure coefficient*, *i.e.*, the coefficient of increase in pressure at constant volume.

The **volume coefficient,** α_v, is defined as *the ratio of the increase in volume of the gas at constant pressure, per degree rise of temperature, to its volume at 0°C*. If v_0 and v be the volumes of a given mass of gas kept at constant pressure at 0°C and t°C respectively, then

$$\alpha_v = \frac{v - v_0}{v_0\, t}$$

Or $$v = v_0(1 + \alpha_v t) \quad \ldots(1)$$

The **pressure coefficient,** α_p, is defined as *the ratio of the increase in pressure of the gas at constant volume, per degree rise of temperature, to its pressure at 0°C.* If p_0 and p be the pressure of a given mass of gas kept at constant volume at 0°C and t°C respectively, en

$$\alpha_p = \frac{p - p_0}{p_0 \, t}$$

Or $$p = p_0(1 + \alpha_p t) \qquad \ldots(2)$$

It is to be carefully noted that the coefficient of expansion α_v and α_p refer to the volume and pressure of the gas at 0°C. In the case of solids and liquids, one could, without serious error, refer to the volume at an initial temperature other than 0°C ; but this cannot be done in the case of gases on account of the interdependence of their volume, pressure and temperature.

Experimental determination of the two coefficients.

1. The **volume coefficient** is estimated by measuring the increase in volume of a given mass of gas maintained at constant pressure due to a given rise in temperature.

Gay-Lussac was one of the first to measure the volume coefficient with a fair degree of accuracy. He used a glass bulb B furnished with a straight stem of thermometer tubing AB, which was carefully calibrated and graduated (Fig. 43). It was then filled with dry air as follows : After filling with mercury it was fitted vertically with the bulb up in a wider tube packed with calcium chloride. Introducing a fine platinum wire into the stem, the mercury was slowly removed, when air made quite dry by passage through the calcium chloride occupied the bulb and stem except for a pellet of mercury left in the stem to act as an index I, marking the volume of air enclosed. The bulb was then arranged in a bath C with the stem perfectly horizontal, so that the pressure of the enclosed air was that of the atmosphere. The

Gay-Lussac

bath was first filled with melting ice and the position of the index in the bulb was noted. Then the bath was gradually heated until the water boiled. The index was read at different temperatures indicated by the thermometer T, as the heating progressed. From these data, the mean coefficient of apparent expansion of air in glass was found, and adding to it the known coefficient of expansion of glass the mean coefficient of absolute expansion α_v was determined as $\cdot 00375 = 1/268$, which is appreciably higher than the correct value. This can be accounted for by two sources of error involved in the apparatus, *viz.*, (*i*) the air enclosed could not have been quite dry, since the moisture clinging to the interior of the bulb and stem was not removed, and (*ii*) the mercury index could not completely isolate the air enclosed from the outside.

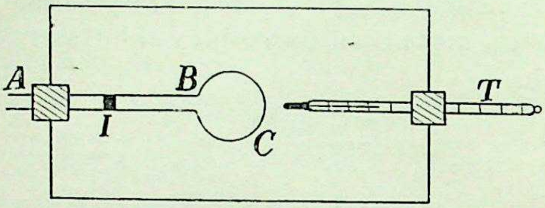


Fig. 43. Gay-Lussac's apparatus.

Regnault, in order to eliminate these errors, modified the technique as follows :—

A bulb A of about 700 c.c. capacity was connected by a capillary tube to a mercury manometer BCD, the limb BC of which was carefully calibrated. The manometer was provided with a stop cock T at its lower bend. A constant temperature water-bath surrounded the manometer. The bulb A was alternately evacuated and filled with dry air several times, in order to remove all traces of moisture inside, the side-tube E being used for that purpose.

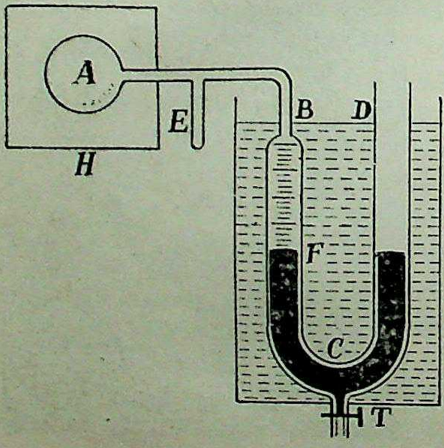


Fig. 44. Regnault's apparatus.

The bulb was first kept in a bath H of melting ice and water, allowing some time for the bulb to acquire the temperature of the bath, *i.e.*, 0°C, and the mercury levels in the manometer were adjusted to be the same so that the presure of the enclosed air was equal to the atmospheric pressure. For making this adjustment easily the quantity of air in the bulb was varied through the tube E, which was then sealed off. The reading of the murcury level F in the calibrated limb was noted. From the known capacities of the bulb, the connecting capillary tube and the portion BF of the calibrated limb of the manometer, the volume of the air enclosed at 0°C could be estimated.

The bath was then heated and its temperature read with a suitable thermometer, standardised on the constant volume hydrogen scale. As the temperature increased the air in the bulb expanded forcing the mercury down in the limb BC and up in CD. At any given temperature, the pressure of the air was restored to its initial value of the atmospheric pressure, by allowing mercury to run out through the stop-cock C until the levels were once again the same and the reading of the level in the calibrated limb was noted. The difference in the two readings of the level gave the increase in volume of the air at constant pressure due to a given rise of temperature. The process was repeated at intervals of 10°C up to the temperature of boiling water. The readings of the level were also taken at the same temperatures when the air was allowed to cool down. The mean values of the two sets of readings thus obtained were used for calculating the volume coefficient. The apparatus could evidently be used for other gases besides air, the side-tube E being used conveniently for filling the bulb with the gas to be investigated.

Regnault using different gases in his apparatus studied the following points with the data obtained :—

To see *whether gases expand uniformly*, unlike liquids, he calculated the mean coefficient of expansion for different ranges of temperature as follows :—

If V, v_1 and v_2 be the volumes of the bulb, the capillary tube and the portion BF of the manometer respectively, assuming that all the above three component parts are at the same temperature,

the volume of the gas at 0°C $= V + v_1 + v_2$

When the temperature of the gas is raised to t°C, let the volume of the manometer occupied by it increase to v_2'. Then

the volume of the gas at t°C $= V + v_1 + v_2'$

The mean coefficient of expansion for the range 0°C and t°C is given by

$$\frac{(V + v_1 + v_2') - (V + v_1 + v_2)}{(V + v_1 + v_2)\,t} = \frac{v_2' - v_2}{(V + v_1 + v_2)t}$$

The relation used by Regnault was much more complicated than the above one, since he took care to correct for the following sources of error :—(*i*) the bulb, the capillary tube and the manometer were all actually at different temperatures ; (*ii*) the expansion of glass of the bulb, etc. As a result of his investigations, calculating the mean coefficient for different ranges, he found *that all gases showed small departures from uniform expansion.*

Next to see *whether different gases have the same coefficient of volume expansion* he calculated the mean coefficients of a number of gases for the range 0°C — 100°C and obtained the following results :—

Air	..	0·0036706
Hydrogen	..	0·0036613
Carbon monoxide	..	0·0036688
Carbon dioxide	..	0·0037099
Sulphur dioxide	..	0·0039028
Cyanogen	..	0·0038767

Thus he found that the *values differed slightly from one another for the various gases* and that none of them was exactly equal to $\frac{1}{273} = 0{\cdot}003662$, except perhaps in the case of hydrogen.

Conducting experiments on air at various constant pressures, he found that there was a *small increase of the volume coefficient as the pressure of the air increased.*

These historical experiments cannot be used as ordinary laboratory methods. We shall now describe one of these methods which is a simplified form of Regnault's technique and gives satisfactory results.

A bulb A is connected through a narrow glass tube bent twice at right angles to a mercury manometer, of which the limb B is calibrated, while the limb C joined to B by rubber tubing is provided with a clamping device so that it can be moved up or down along a vertical stand (Fig. 45). The bulb is put in a cold water bath whose temperature t_1 is noted. After allowing it to stand for some time so that it acquires the temperature of the bath, the limb C is adjusted until the mercury stands at the same level in the two limbs, using the tap T, if need be. The reading of the mercury level in B is noted. The bath is heated, when the enclosed air expands pushing down the mercury level in B and up in C. Maintaining the bath at any given temperature t_2, the limb C is lowered until the mercury is at the same level in both the limbs. The reading of the level in B is again noted. The difference between the two readings gives the increase in volume of the air at constant pressure, *i.e.*, of the atmosphere.

The process is repeated, maintaining the bath at temperatures spaced at 10° increase, up to 100°C, and again at intervals of 10°C decrease allowing the bath to cool down The mean values of the two sets of readings are used for calculating the volume coefficient.

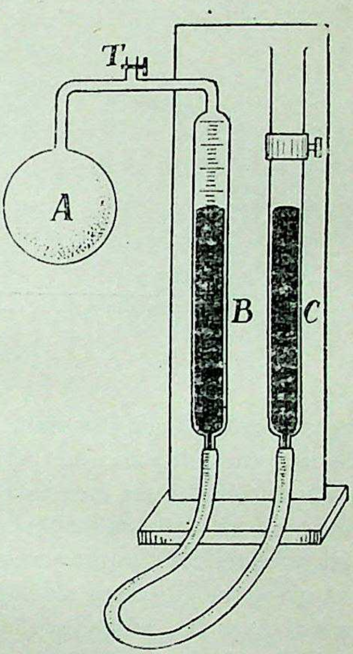


Fig. 45. Volume coefficient apparatus.

Although we have insisted that in the cases of gases we must refer to the initial volume at 0°C, we have not done so here. Still, by taking the data for any two temperatures, the coefficient can be obtained quite accurately as follows :—

Knowing the capacity of the bulb and the connecting tube (which is independently determined) and adding to it the volume occupied by air in the graduated limb B (which is directly read), the volume of the enclosed air at any temperature can be readily found.

Let v_1 and v_2 be the volumes of the air enclosed at temperatures t_1 and t_2 respectively.

Then $$v_1 = v_0 (1 + \alpha_v t_1)$$
and $$v_2 = v_0 (1 + \alpha_v t_2)$$
where v_0 is the volume at 0°C.

$$\frac{v_1}{v_2} = \frac{1 + \alpha_v t_1}{1 + \alpha_v t_2}$$

$$\therefore \qquad \alpha_v = \frac{\quad - v_1}{v_1 t_2 - v_2 t}$$

α_v is calculated from different ranges of temperature and the average value is found.

α_v can be determined also graphically. Using the volumes of the enclosed air at different temperatures, a graph is drawn connecting volume and temperature. The experimental points are found to lie on a straight line, showing that when the pressure is kept constant the volume of a gas increases uniformly with the temperature (Fig. 46). When the straight line graph is produced backwards to cut the temperature axis at A corresponding to zero volume, the intercept OA gives the absolute zero of temperature (— 273°C), and its reciprocal gives the volume coefficient. Since all gases become liquids or solids much above -- 273°C, the point A cannot be experimentally checked.

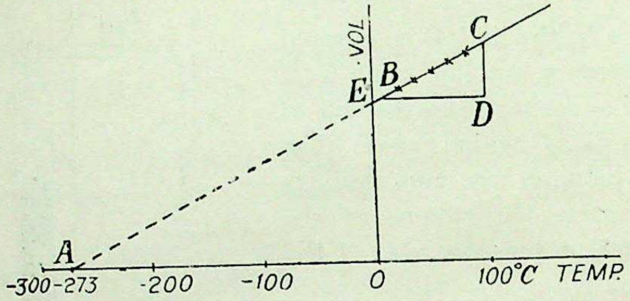


Fig. 46.

But from the graph, the rate at which the volume increases with the temperature and the volume at 0°C can be found using the experimental points. The former is evidently equal to CD/BD and the latter to OE, and dividing one by the other, the volume coefficient is obtained.

2 The **pressure coefficient** can be determined by measuring the increase in pressure of a given mass of gas at constant volume due to a given rise in temperature.

The ordinary laboratory method, which makes use of a simple arrangement similar to the one described above but with certain modifications for maintaining the volume constant and known as *Joly's apparatus*, is capable of giving results to an accuracy of about one per cent. It consists of a bulb A containing dry air, connected through a narrow glass tube bent twice at right angles to a mercury manometer mounted on a vertical stand. The limb B of the manometer carries a file mark X at its top end while the limb C joined to B by rubber tubing can be slid up and down and fixed at any position on the stand. By maintaining the level of mercury in B always against the mark X, the volume of the enclosed air is kept constant. A metre scale S is fixed to the vertical stand to read conveniently the mercury levels in the manometer (Fig. 47).

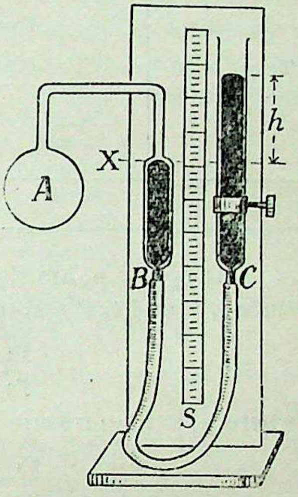


Fig. 47. Joly's apparatus.

The bulb is completely immersed in a cold water bath and after allowing some time for the bulb and enclosed air to acquire the temperature of the bath, the temperature of the bath is noted (after stirring well the water) with a thermometer calibrated on the constant volume hydrogen scale. The limb C of the manometer is raised or lowered in order to bring the level of mercury in B against the mark X and clamped in that position. The difference between the mercury levels (h) in the two limbs is measured with the [illegible] of the scale S. If H is the reading of Fortin's barometer which gives the atmospheric pressure, the pressure of the air in the bulb at the temperature of the bath is given by

$$p = \mathrm{H} \pm h$$

according as the level in C is above or below that in B *i.e.*, above or below X.

The bath is then steadily heated and its temperature is successively maintained (by suitably using the heater) at intervals of 10, 20, 30°C, etc. above the initial temperature up to the boiling point of water. At each of these temperatures, the manometer is adjusted to have the mercury level in the closed limb B against X and the difference of levels noted.

After thus reaching the boiling point of water, the bath is allowed to cool down and observations are made at the same temperature as before. The pressure of the air enclosed at any one of the temperatures is taken as the mean of the readings taken at that temperature while heating the bath and while cooling it, as indicated on the next page :—

Reading of level X = ...

Reading of Fortin's barometer H = ...

Temp. in °C	Readings of mercury level in C			h	Pressure of air $H \pm h$
	Temp. rising	Temp. falling	Mean		

If p_1 and p_2 are the pressures of the enclosed air at two temperatures t_1°C and t_2°C respectively, then

$$p_1 = p_0 (1 + \alpha_p t_1)$$

$$p_2 = p_0 (1 + \alpha_p t_2)$$

where p_0 is the pressure of the air at 0°C.

$$\frac{p_1}{p_2} = \frac{1 + \alpha_p t_1}{1 + \alpha_p t_2}$$

$$\therefore \qquad \alpha_p = \frac{p_2 - p_1}{p_1 t_2 - p_2 t_1}$$

Using this relation, α_p is calculated for different ranges of temperature and the average value is found.

α_p can be determined also graphically. A graph is drawn connecting pressure and temperature, as in the case of volume and temperature. The line joining the experimental points is found to be straight which when produced backwards cuts the temperature axis at about −273°C corresponding to zero pressure. The intercept, as before, gives the absolute zero and its reciprocal gives the pressure coefficient. From the graph, the rate of increase of pressure with temperature and the pressure at 0°C can be readily found and the former divided by the latter gives the pressure coefficient. The straight graph indicates that the pressure of a gas at constant volume increases uniformly with temperature.

The main defect of the method is that the whole volume of the gas is not at the same temperature as that of the bath, the gas in the connecting tube being evidently cooler.

Regnault undertook a more accurate determination of the pressure coefficient of not only air but also other gases with an improved apparatus, similar to the Harker and Chappuis constant volume thermometer (*Cf.* p. 25). He made adequate corrections both for the expansion of the bulb and for the fact that the gas in the "dead space" was not at the same temperature as that in the bulb. He found that the pressure at constant volume did not increase quite uniformly with temperature in the case of several gases he studied, except hydrogen. Calculating the mean pressure coefficient for the range 0°C to 100°C for different gases, he obtained the following values :—

Air	...	0·003674
Hydrogen	...	0·003663
Nitrogen	...	0·003675
Carbon dioxide	...	0·003725

These results showed that in no case the value was exactly equal to $\frac{1}{273}$ and that the different gases had slightly different values.

Conducting a series of experiments to find the pressure coefficient when the pressure was varied over a wide range, he found that α_p gradually increased as the pressure of the gas increased. The results obtained by him for air is given below :—

Pressure at 0°C	Pressure at 100°C	α_p
109·72 mm.	149·31 mm.	0.0036482
174·36 ,,	237·17 ,,	0·0036513
266·06 ,,	395·07 ,,	0·0036542
374·67 ,,	510·35 ,,	0·0036587
760·00 ,,	1038·54 ,,	0·0036650
1678·60 ,,	2286·09 ,,	0·0036760

Results. The results of the researches on the volume and pressure coefficients of gases may now be summed up :—

1. Although careful and accurate measurements reveal small differences in the value of the volume coefficient for different gases, the variation is small, unlike in the case of solids and liquids.

2. To a first approximation all gases have the same volume and pressure coefficients which are numerically equal to each other, with a value of $\frac{1}{273}$. This is found to be the case chiefly with the so-called permanent gases, such as air, hydrogen and nitrogen, which are far removed from their liquefying points, while the more easily condensible gases, such as carbon dioxide, show more marked departures. The constancy and equality of the two coefficients, which have been rightly surmised as a consequence of Boyle's law, have led to the more general Charles' law, as we have already seen in the previous chapter.

3. The discrepancies concerning the values of the two coefficients for different gases and for different pressures and the slight non-uniformity of change of volume and pressure with temperature imply that all gases do not obey the Boyle's and Charles' laws with the same degree of accuracy. Concerning this deviation of gases from the above laws, Holborn and Otto have proposed the empirical relation :

$$pv = \mathrm{RT} + \mathrm{B}p + \mathrm{C}p^2 + \mathrm{D}p^3 + \ldots\ldots$$

where B, C, D are functions of temperature, being constant at constant temperature, whose values decrease rapidly. According to this relation, at infinitely low pressure ($p \rightarrow 0$) all gases will obey the ideal gas law $pv = \mathrm{RT}$ accurately. It is experimentally found that the temperature scales, obtained by using different gases and extrapolating to zero pressure are identical. This is the ideal gas scale. The coefficient of expansion for an ideal gas can be calculated in this way from the data given by Heuse and Otto. The mean of several observations gives $\alpha_v = 0{\cdot}0036608 = 1/237{\cdot}16$. Although the ideal gas cannot be realised in practice, it presents the behaviour common to all gases at infinitely low pressure, when they all obey Boyle's law strictly and have the same volume and pressure coefficients equal to $1/273{\cdot}16$. We shall see later how the deviations of actual gases from Boyle's law receive a ready explanation on the kinetic theory and how Van der Waals' equation gives a more satisfactory description of actual gases than the perfect gas equation.

Practical Applications. The chief application of the expansion of gases is *gas thermometer*, which we have already dealt with in the previous chapter. Another important application is the *production of low temperature* by subjecting gases to very high pressures and liquefying them, which will be considered later.

QUESTIONS

1. Describe an interference method of determining the coefficient of linear expansion of a solid. (*Madras University*)

2. Discuss the measurement of the coefficient of expansion of crystals and state briefly the character of the results obtained.

3. If a crystal has a coefficient of expansion of 13×10^{-7} in one direction and 231×10^{-7} in every direction at right angles to the first, calculate its coefficient of cubical expansion. (**Ans.** 475×10^{-7}) (*London B.Sc.*)

4. Describe, in full detail, the method by which the expansion of crystals, when heated, may be studied experimentally. (*Allahabad University 1943 ; Aligarh University 1949 ; Punjab University 1946, 1954*)

5. Describe and explain the interference method for finding the coefficient of thermal expansion of crystals.

How does the thermal expansion of a crystal differ from that of an ordinary metal. *(Punjab University 1961)*

6. Discuss the comparator method for finding the coefficient of linear expansion of a solid. Compare and contrast it with Roy and Ramsden's method.

7. Explain the methods adopted for the compensation for effects of temperature in pendulum clocks and balance wheels of watches. *(Madras University)*

8. A clock with a metal pendulum beating seconds keeps correct time at 0°C. If it loses 10 secs. a day at 20°C, calculate the coefficient of linear expansion of the pendulum. (**Ans.** 5×10^{-5}) *(Madras University)*

9. A lump of quartz which has been fused is suspended from a quartz fibre and allowed to oscillate under the influence of the torsion of the fibre. If the coefficient of linear expansion of the material is 7×10^{-7} and the temperature coefficient of its rigidity is $+ 13 \times 10^{-5}$ how many seconds a day would a change of temperature of 1° C make ? (**Ans.** 5·646 secs. per day gain per °C rise). *(London B.Sc.)*

10. Write notes on :—

(*a*) Expansion of crystals. *(Madras University ; Delhi University)*

(*b*) Superficial expansion. *(Madras University)*

11. Show that the increase in volume of a hollow cylindrical vessel heated through a given range of temperature is equal to that of a solid cylinder of the same material and dimensions heated through the same range. *(Madras University)*

12. Distinguish between coefficient of absolute and apparent expansion of a liquid. Describe a method of finding the coefficient of volume expansion of a solid using a pyknometer. *(Madras University)*

13. Describe a method by which the cubical expansion of a liquid can be accurately determined by weighing a solid of known expansion in it at two known temperatures.

A solid is found to weigh 29·9 gms. in a liquid of specific gravity 1·21 at 10°C, its weight in air being 45·6 gms. It weighs 30·4 gms. in the same liquid at 25°C when its specific gravity is 1·17. Calculate the coefficient of cubical expansion of the liquid. (**Ans.** $0{\cdot}8 \times 10^{-4}$).

14. Describe Regnault's method for the determination of the coefficient of absolute expansion of mercury. Indicate briefly the precautions taken by Regnault to avoid errors.

If the coefficient of cubical expansion of glass and mercury are $2{\cdot}5 \times 10^{-5}$ and $1{\cdot}8 \times 10^{-4}$ respectively, what fraction of the whole volume of a glass vessel should be filled with mercury in order that the volume of the empty part should remain constant when glass and mercury are heated to the same temperature ?

(**Ans.** 5/36). *(Dacca University)*

15. Define absolute coefficient of expansion of a liquid. How is this coefficient determined in the case of mercury ? *(Madras University)*

16. Describe Regnault's method of finding the absolute coefficient of expansion of mercury, explaining the calculations involved in it. Why is this method better than others ? (*Madras University* ; *Calcutta University, 1949*)

17. Describe a method of finding the coefficient of absolute expansion of a liquid. Show that the coefficient of apparent expansion of a liquid is very nearly equal to the difference between the coefficient of absolute expansion of the liquid and the coefficient of cubical expansion of the material of the containing vessel. (*Cambridge*)

18. If l is the coefficient of linear expansion of a solid, explain carefully why $3l$ may be used as the coefficient of cubical expansion.

The height of a mercury barometer read with a steel scale is 754 millimetres at 20°C. What will it read at 0°C ? (Coefficient of linear expansion of steel 0·00012 per °C and coefficient of cubical expansion of mercury 0·000182 per °C). (**Ans.** 751·5 mm.) (*Oxford*)

19. If ρ_0 is the density of a liquid at 0°C and ρ_t at t°C, show that

$$\rho_t = \frac{\rho_0}{1 + \alpha t}$$

where α is the coefficient of absolute expansion of the liquid. (*Madras University*)

20. Give a critical account of the experiments which have been made to find the temperature of the maximum density of water. Discuss their bearing on the units of mass and volume.

21. The difference between the fixed points of a mercury thermometer is 18 cm. If the volume of the bulb and capillary tube up to the 0° mark is 0·9 c.c. calculate the sectional area of the capillary. Coefficient of cubical expansion of mercury $= 1{\cdot}8 \times 10^{-4}$, coefficient of linear expansion of glass $= 7 \times 10^{-6}$. (**Ans.** 0·000805 sq. cm.). (*Madras University*)

22. Devise a method of measuring the coefficient of cubical expansion of a solid of which only a small quantity is available and which cannot be polished.

23. Distinguish between the absolute and relative expansion of a liquid and describe how you would determine the relative expansion of mercury in glass. Show how the coefficient is calculated from the measurement made. (*Oxford*)

24. A long glass tube with a uniform capillary bore has in it a thread of mercury which is 1 metre long at 0°C. What will be it length at 100°C, if the real coefficient of expansion of mercury is 0·000182 and the coefficient of cubical expansion of glass = 0·000025. (**Ans.** 100·52 cms.). (*Madras University*)

25. Why does the balancing of a hot against a cold column eliminate the expansion of the vessel ? If the cold column at 4°C is 60 cm. high and the hot column at 95°C is ½ cm. higher, what is the co efficient of absolute expansion of the liquid ?

26. A block of quartz of mass 13·5 gms. is weighed in aniline at 0°C and at 100°C. The weighings are 8·905 and 9·29 gms. respectively. Calculate the coefficient of cubical expansion of aniline, assuming the coefficient of cubical expansion of quartz to be zero. (**Ans.** 0·00098) (*Madras University*)

27. How would you find the volume and pressure coefficients of a gas ?

A thousand c.c. of air at 50°C is cooled down to 10°C and at the same time the external pressure upon the air is increased from 750 mm. to 765 mm. What is the volume reduced to, the coefficient of expansion of air for 1°C being 0·00366 ? (**Ans.** 859 c.c.)

28. An air bubble rises from the bottom of a pond, where the temperature is 7°C, to the surface 27 metres above, at which the temperature is 17°C. Find the relative diameters of the bubble in the two positions, assuming that the pressure at the pond surface is equal to that of a column of mercury of density 13·6 gms. per c.c. and 76 cm. in height. (**Ans.** 1·55 : 1)

29. In a determination of the coefficient of expansion of air by Gay-Lussac's method the volume of the air in the tube was found to be 240 c.c. at 0°C and at 77°C, its apparent volume was 310 c.c. Find the volume obtained for the required coefficient. The mean coefficient of cubical expansion of glass is 0·000026. (**Ans.** 0·0038)

30. Explain the meaning of the expression *coefficient of expansion* of a gas. Supposing that a quantity of gas were to occupy 500 c.c. at 80°C and 600 c.c. at 120°C, what would be its coefficient of expansion ? (**Ans.** $\frac{1}{120}$)

31. Describe, in detail an experiment for determining the pressure coefficient of air in the range 0° to 100°C.

A thin bulb containing air at 41°C, is sealed up and placed in an oil bath. The bath is heated gradually until the bulb bursts at 198°C. Find in atmospheres the bursting pressure of the bulb. (**Ans.** 1·5 atmospheres).

CHAPTER III

THERMAL CAPACITY—SPECIFIC HEAT

Introduction. When a hot body is put in contact with a cold one, the former gets colder and the latter warmer. From this observation it is natural to conclude that a certain *quantity of heat* has passed from the hot body to the cold one. It is also usual to speak of the *flow of heat* from the hot body to the cold one on the analogy of the flow of a liquid from a higher level to a lower one or the flow of electric current from a point of higher potential to that of lower potential. Just as difference of levels starts the flow of a liquid or difference of potentials the flow of an electric current, so also difference of temperatures causes the flow of heat. Hence heat can be conceived as a *physical entity* (like a liquid or an electric current), which causes a rise in temperature of any body to which it is given. Heat and temperature are like cause and effect : change of temperature is actually observed, while flow of heat is only inferred. It is to be noted also that just because heat flows from one body to another, it need not be concluded that heat is an invisible fluid, as the ancients did. We shall postpone the study of the exact nature of heat to a later chapter and attend here only to methods of defining and measuring quantity of heat.

Everyday experience and simple experiments show that the quantity of heat gained or lost by a substance is proportional to the mass and nature of the substance as well as to its change of temperature. Thus, for example, a greater quantity of heat is required to raise a large mass of water from 0°C to 100°C than to raise a small mass through the same range of temperature. The amount of heat required to raise the same mass of water to different temperatures varies proportionately. When equal masses of different substances, say, lead, copper and aluminium, heated to the same rise of temperature are dropped in equal quantities of water, the equilibrium temperature of the mixture is found to be different in the three cases, being lowest for lead and highest for aluminium. This shows that equal masses of these substances, though heated to the same temperature, take in different quantities of heat, so that they share with the same amount of water different quantities of heat. Hence they have different capacities for heat.

These observations can be analytically expressed by the relation

$$Q = ms\theta \qquad \ldots(1)$$

where Q is the quantity of heat gained or lost by a substance, m its mass, s a constant depending on its nature and θ the change of temperature.

Unit of heat. A unit for measuring quantities of heat can be readily obtained from the above relation, by putting $m = 1$, $s = 1$, $\theta = 1$ and assuming a standard substance like water to have $s = 1$. Hence the unit quantity of heat is the *amount of heat required to raise one gram of water through one degree centigrade*. It is called the *calorie*.

This definition presumes that the same amount of heat is required to raise one gram of water through 1°C at any temperature. But accurate measurements show this not to be the case. Hence, in precision work, one must specify either the *mean calorie* which is the average amount of heat required to raise 1 gram of water through 1°C over the temperature range considered or some definite temperature. This has led to the following units :—

(*i*) The amount of heat necessary to raise 1 gram of water from 0°C to 1°C (used by Regnault).

(*ii*) The amount of heat necessary to raise 1 gram of water from 14·5°C to 15·5°C—this is known as the *15°C calorie*, recommended by the International Union of Pure and Applied Physics as the standard unit.

For all ordinary purposes, however, the calorie is defined as the heat necessary to raise the temperature of 1 gram of water through 1°C at any temperature.

As the calorie represents a small quantity of heat, a larger unit called the *major calorie*, equal to 1,000 calories is used for industrial purposes, chiefly in Europe. In England, another unit, known as the *British thermal unit* (B.Th.U.) is largely employed, which is the amount of heat necessary to raise 1 lb. of water through 1°F. Since 1 lb. = 453·6 grams, and 1°F = 5/9°C, the B.Th.U. = 453·6 × 5/9 = 252 calories.

Thermal capacity. Since different substances have different capacities for heat, as indicated above, they can be distinguished by a quantity known as *thermal capacity* of a body which is defined as the amount of heat required to raise the temperature of the body through one degree centigrade. If m grams be the mass of the body and s its characteristic constant, referred to in relation (1), its thermal capacity is ms calories.

Specific heat. The constant 's' mentioned above is known as the *specific heat.* Supposing that a given mass of water requires a quantity of heat Q_1 to raise its temperature by θ, and that the same mass of any other substance requires a quantity of heat Q_2 for the same rise in temperature, applying relation (1) we have

$$Q_1 = m \times 1 \times \theta$$

$$Q_2 = m \times s \times \theta$$

$$\therefore \qquad s = \frac{Q_2}{Q_1} \qquad \ldots (2)$$

Hence the specific heat of a substance can be defined as the ratio of the quantity of heat required to raise the temperature of a given mass of the substance through a given temperature range to the quantity of heat required to raise an equal mass of water through the same temperature range.

Since the unit of heat is the quantity of heat required to raise 1 gram of water through 1°C, the specific heat of a substance is usually defined in terms of that unit, as *the number of units of heat required to raise unit mass of the substance through one degree centigrade.* It is thus the thermal capacity of unit mass of the substance. In the C.G.S. system it is expressed in calories per gram. It is now readily seen that the specific heats of different substances are different and that of water is unity.

As the specific heat is strictly a ratio, it is merely a number that remains the same in whatever system (C.G.S. or F.P.S.) heat is measured.

Just like in the case of water, the specific heat of other substances is not strictly the same at all temperatures. Hence it is usual to distinguish between *meun and true specific heats* of a substance. If a quantity of heat Q raises the temperature of m grams of a substance from θ to θ', the *mean specific heat* is given by the relation

$$s = \frac{Q}{m(\theta' - \theta)} \qquad \ldots (3)$$

If dQ is the amount of heat required to raise the temperature of the substance through an infinitely small range $d\theta$ at the temperature θ, the *true specific heat* at the temperature θ is given by

$$s = \frac{1}{m} \cdot \frac{dQ}{d\theta} \qquad \ldots (4)$$

It is usually the mean specific heat that is determined experimentally.

Water equivalent of a body. The thermal capacity of a body ms represents also its water equivalent, since the specific heat of water is unity. Thus ms grams of water and m grams of a body of specific heat s have the same thermal capacities. This mass of water having the same thermal capacity as the body is called the *water equivalent of the body* and is defined as *the mass in grams of water which has the same thermal capacity as the body*. It is to be noted that the product of the mass and specific heat of a body expressed *in calories* gives the thermal capacity, while expressed *in grams* its water equivalent.

Calorimetry. The measurement of the quantity of heat and hence of specific heat has been called calorimetry, since the unit chosen is the calorie. The basic principle of calorimetry is *conservation of heat*. When a hot body cools, the surrounding bodies are observed to show a slight rise in temperature. Hence it is legitimately assumed that the *heat lost* by the cooling body is equal to the *heat gained* by those which are warmed, or, in general, the quantity of heat present is conserved. We shall see in a later chapter that the conservation of heat is merely a particular case of the universal law of conservation of energy, since heat and energy are equivalent.

Calorimetry may be classified under two general heads, according to the devices employed for measuring quantites of heat :—

1°. *Change of temperature or thermometric calorimetry.* Since this method essentially depends on changes of temperature, the thermometer becomes the instrument of prime importance ; the unit employed is the calorie.

2°. *Change of state or latent heat calorimetry.* This method depends on the latent heat of fusion or evaporation. It is a matter of common experience that a considerable quantity of heat is absorbed or given out when matter changes its state from solid to liquid and from liquid to gas or *vice versa*. Thus a large amount of heat is needed to convert ice at 0°C into water at 0°C, to convert water at 100°C into steam at 100°C. In the reverse process, when steam is condensed or water converted into ice, a great quantity of heat is given out. Since the quantity of heat involved in these changes of state is not manifested as a rise of temperature, it is said to be hidden or *latent* in the matter undergoing the change. We shall describe in the next chapter methods of determining these latent heats. For the present, it is enough to note that as the latent heat calorimetry deals with fixed temperatures of fusion or evaporation it does not essentially involve the use of a thermometer. Further the unit of heat employed is the latent heat L, which is the quantity of heat required to convert *either* 1 gram of ice at 0°C into water at 0°C *or* 1 gram of water into steam at the boiling point (100°C). The latent heat of steam is several times greater than that of ice, the former being about 540 calories while the latter about 80 calories. This type of calorimetry was much used at a time when accurate measurement of temperature was not yet devised. But with the introduction of precision thermometers and electrical heaters, it is now less in use, chiefly on account o its inherent drawbacks.

In practice, the following are the chief methods employed in calorimetry :—

(*a*) *Method of mixtures.* It is the oldest and most convenient laboratory method, that can be used in the case of solids, liquids and gases. As early as 1840, Regnault made careful researches on this method and obtained results of great accuracy. The basic principle of the method is *conservation of heat*, *i.e.*, mixing suitably a hot body with a cold one, the heat lost by the hot body is equated to the heat gained by the cold one. An important source of error in this method is the heat lost by conduction, convection and radiation, which has to be either eliminated or corrected for. Such a correction is ordinarily known as *radiation correction*, although in reality the loss of heat through conduction and convection is much more serious than through radiation. The method of correction is based on an empirical law discovered by Newton, hence called *Newton's law of cooling* which states that the rate of loss of heat of a hot body is proportional to the difference of temperature between the body and its surroundings ; it can be expressed analytically as $-(dQ/dt) = K\theta$, here $-dQ$ is the heat lost in a time dt when the difference of temperature between the hot body and the surroundings is θ, and K a constant of proportionality depending only on the area and nature of the cooling surface. It is to be noted that the above law is true only when the difference of temperature is not very great (*i.e.*, within 30°C about) and when the hot body is [illegible] (*b*) *Method of cooling.* This method is well suited in the case of liquids, but not for solids or gases since they cannot be stirred to keep the temperature uniform in order to have constant cooling conditions. It is based on the assumption that when a hot body cools in a given enclosure, the rate of cooling is governed by a general law of the form

$$-\frac{dQ}{dt} = K \cdot f(\theta)$$

where K is a constant depending on the area and nature of the cooling surface, $f(\theta)$ is an unknown function of θ, the excess of temperature of the body over that of the surroundings. It is not the same as Newton's law of cooling which assumes that $f(\theta) = \theta$, but a general one, where $f(\theta)$ need not necessarily be a simple algebraic or trigonometric function of θ. No radiation correction is to be applied in this method, since it is based on cooling itself.

(*c*) *Electrical method.* This method was first devised by Joule to measure the mechanical equivalent of heat and then perfected by many workers, such as the Griffiths, Schuster and Gannon, Jaeger and Steinwehr, Callendar and Barnes and others to yield results of great accuracy. It is applicable to solids, liquids and gases and is based on the simple relation $Q = ms\theta$.

A measured quantity of electrical energy is converted into heat and the rise in temperature of a known mass of material is observed. If the heat Q is generated by passing a current I through a wire of resistance R under a potential difference E, the electrical energy used in a time t is EIt or I^2Rt. If this raises the temperature of a mass m of a substance of specific heat s through $\theta°$,

$$Q = \frac{EIt}{J} = \frac{I^2Rt}{J} = ms\theta$$

where J is the mechanical equivalent of heat. This method ordinarily requires radiation correction.

(*d*) *Method depending on latent heat.* This method is naturally sub-divided into two :—

(*i*) *Method of melting ice,* where the heat Q given out by a hot body is used to melt ice and thereby measured by the amount of the ice melted. If m gms. of a hot substance of specific heat s and temperature θ melts M gms. of ice, we have,

$$Q = ms\theta = ML$$

where L is the heat of fusion. The initial researches conducted by Black, Lavoisier and Laplace utilising this method did not give good results, due to imperfect designs of apparatus. Bunsen was able to device an improved form of apparatus, known as the *Bunsen's ice calorimeter* which was used in the measurement of specific heat of rare metals available only in small quantities. An inherent defect of the method lies in the fact that a given sample of water can freeze into ice of different densities.

(*ii*) *Method of condensation of steam*, where the heat Q necessary to raise the temperature of a cold substance from its initial temperature to that of steam is measured by the amount of steam condensed into water at the same temperature. The fundamental relation to be used is similar to the previous case, *viz.*,

$$Q = ms\theta = ML,$$

where m is the mass of the substance, s its specific heat, θ the difference between the initial and final temperature of the substance, M the mass of steam condensed into water and L the latent heat of steam. Joly was the first in 1886 to devise an apparatus employing this method, known as *Joly's steam calorimeter*, which was used to determine the specific heat of rare substances obtainable only in small quantities. In 1889, he improved the apparatus into what is known as the *differential steam calorimeter*, with which the specific heat of gases at constant volume was determined. A number of precautions and corrections are found necessary to get accurate results by this method.

EXPERIMENTAL DETERMINATION OF SPECIFIC HEAT

The specific heat of a substance differs in the three states, solid, liquid and gas. Water offers a typical example : ice — 0·5, water — 1 and steam — 0·477. In general, the specific heat in the solid and gas states is much smaller than in the liquid state. Of the methods employed in the determination of specific heat, some are common to solids, liquids and gases, while others are best suited either to only one of them or to two of them. For the sake of clarity, we shall deal with the determination of the specific heats of solids, liquids and gases under separate heads.

SPECIFIC HEAT OF SOLIDS

1. Method of mixtures is the one most commonly used in the laboratory for determining the specific heat of solids. The apparatus first devised by Regnault for this purpose consists of two parts, the heater and the calorimeter (Fig. 48). The heater consists of an air-chamber surrounded by two coaxial cylinders, the annular space between them being supplied with a steady flow of steam. The top of the air-chamber (the inner cylinder) is closed with a cork while the bottom by a trap-door through which the solid may be dropped into the calorimeter. The calorimeter is a copper vessel, nickel plated and polished on the outside, supported on pointed pieces of wood or by means of strings inside a wooden box packed with cotton-wool and provided with a wooden lid, these precautions being taken to reduce loss of heat by radiation, conduction, etc. The heater is separated from the calorimeter by a wooden screen for the same purpose. The calorimeter is provided with a copper stirrer and a sensitive thermometer.

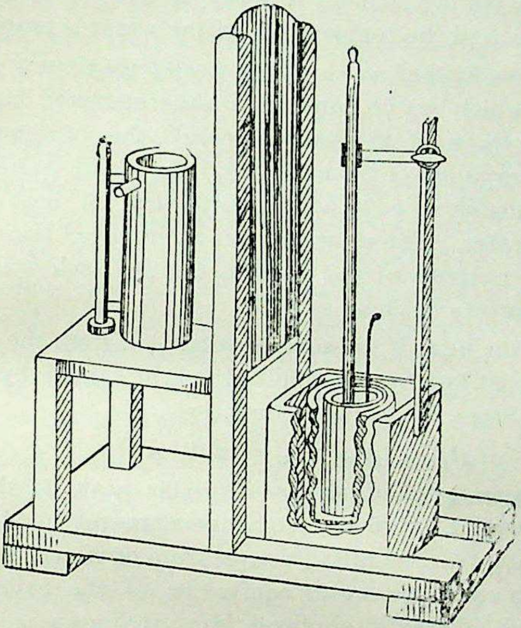


Fig. 48. Regnault's apparatus.

The solid, in the form of a small piece, is weighed carefully and suspended inside the heater by a thread passing through the cork. Steam is passed through the heater from a boiler, so that the solid may be heated without actual contact with steam or water. While the solid is getting heated, the empty dry calorimeter, with the stirrer is weighed. Water is taken in the calorimeter, the amount being just enough to immerse completely the solid when dropped into it, and the calorimeter and contents are weighed again. The mass of water taken is then readily found. The calorimeter is placed back inside the wooden box and the temperature of the water is noted.

When the solid has attained the steady maximum temperature of the heater, which can be noted with a thermometer inserted in the heater close to the solid, the screen is raised, the calorimeter is pushed under the trap-door of the heater and the solid quickly dropped into the calorimeter, so as to have as little loss of heat as possible during the transfer. The calorimeter is then moved back, the screen lowered. The contents of the calarimeter are well stirred and the highest temperature reached is noted.

The specific heat of the solid is calculated from the data taken, equating the heat lost by the solid to the heat gained by the calorimeter and contents, *i.e.*, using the relation

$$ms\,(t_2 - t_1) = (m_1 + w)(t_1 - t)$$

where m is the mass of the solid, s its specific heat, t_2 the temperature of the hot solid, t_1 the highest temperature reached by the calorimeter and contents, t the initial temperature of water, m_1 the mass of water taken and w the water equivalent of the calorimeter and contents, which is readily obtained from the mass of the empty calorimeter and the known specific heat of the material (copper) of the calorimeter.

Radiation correction. In spite of the precautions taken (stated above) to minimise the loss of heat due to cooling when the calorimeter is hotter than the surroundings, the final temperature observed will be less than it ought to be. To obtain accurate results, this error caused by radiation must be corrected for. The correction can be made in the following different ways :—

(*i*) *Elimination.* One way of doing this, first suggested by Rumford, consists in adjusting the initial temperature of the water in the calorimeter to be as far below the room temperature as the final temperature (determined by a preliminary experiment) is expected to be above it. Thus the gain of heat in the first part of the experiment is roughly compensated by the loss of heat in the second part. Another means of elimination of the error is to surround the calorimeter with a constant temperature enclosure, instead of the wooden box packed with cotton wool and keep the temperature of the enclosure always equal to that of the calorimeter by electrical heating.

(*ii*) *Approximate method of correction.* A stop-watch is started at the same time as the hot solid is dropped into the calorimeter. The time taken for the temperature to reach the maximum value is noted. The calorimeter is then allowed to cool for an equal interval of time and the fall in temperature x is found. Then $x/2$ gives the approximate correction which is to be added to the observed maximum temperature.

(*iii*) *Barton's method of correction* based on Newton's law of cooling (which can be legitimately used since the final temperature never exceeds the initial temperature by 30°C in calorimeter experiments), is capable of giving an accurate estimate of the loss of heat by radiation. A stop-watch is started at the same time as the hot solid is dropped into the calorimeter and the temperature readings are recorded at intervals of half a minute until the maximum temperature is reached. The temperature observations are continued for a few minutes more as the calorimeter cools down.

From these readings a time-temperature graph is plotted, taking time on the X-axis and the temperature on the Y-axis, as shown in Fig. 49. Through the point A representing the room temperature the line AEF is drawn parallel to the time-axis. Lines BE and CF, perpendicular to AEF, are also drawn respectively from B, the highest point of the curve corresponding to the maximum temperature observed and from C another convenient point beyond B. From B a line BD is drawn parallel to the time-axis and FC is produced to cut it at D. The choice of the point C must be such that CD = δt is about 1°C and the area BCFE is at least as big as the area ABE.

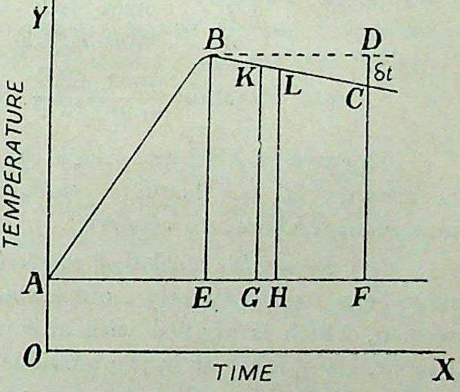


Fig. 49.

Considering a very small interval of time GH if dQ be the amount of heat lost during that interval, the rate of loss of heat at the instant represented by G is equal to dQ/GH. By Newton's law of cooling dQ/GH is proportional te the ordinate GK which gives the excess of temperature of the body over the surroundings at the instant considered,

$$i.e., \qquad \frac{dQ}{GH} \propto GK$$

$$\text{or} \qquad dQ \propto GH \times GK \propto \text{area GKLH}$$

$$\therefore \qquad dQ = k \times \text{area GKLH, where } k \text{ is a constant.}$$

From this, it follows that the heat lost in the interval of time EF is given by

$$Q = k \times \text{area EBCF}$$

If c is the thermal capacity of the calorimeter and contents,

$$Q = c \, . \, \delta t$$

$$\therefore \qquad c \, . \, \delta t = k \times \text{area EBCF} \qquad \dots (1)$$

Arguing in a similar manner for the interval AE, if $\delta t'$ is the loss in temperature during that time, which is, in fact, the required radiation correction, we get

$$c \, . \, \delta t' = k \times \text{area ABE} \qquad \dots (2)$$

Dividing (2) by (1)

$$\frac{\delta t'}{\delta t} = \frac{\text{area ABE}}{\text{area EBCF}}$$

$$\therefore \qquad \delta t' = \frac{\text{area ABE}}{\text{area EBCF}} \times \delta t$$

The area of ABE and EBCF can be readily measured ; δt also is known ; $\delta t'$ is, therefore, calculated ; it is added to be the maximum temperature observed.

(*iv*) *Regnault's method of correction.* Regnault made use of a more accurate but slightly more elaborate method of radiation correction, which is applied with advantage in the case of solids, like rubber, glass, etc. As in the previous method, from the moment the solid is dropped into the calorimeter temperature readings are taken with a sensitive thermometer reading to 1/10°C, at intervals of half a minute, until the calorimeter reaches the maximum temperature and then cools down, say by 1°C.

Let θ be the room temperature, t_1 the maximum temperature observed and n the total number of half minute intervals taken to cool down by 1°C. Then the rate of cooling per interval at the mean temperature $\frac{t_1 + (t_1 - 1)}{2}$ °C is $\frac{1}{n}$, while it is zero at θ°C. According to Newton's law the rate of cooling is proportional to the mean difference of temperature between the cooling body and the surroundings. Hence a straight line graph is drawn with temperature along the X-axis and rate of cooling per interval along the Y-axis with the above two data, from which the rate of cooling corresponding to the mean temperature for any interval recorded can be found.

The correction for radiation is then made as follows :—

Time interval	*Initial temp.*	*Final temp.*	*Mean temp.*	*Rate of cooling from graph*	*Correction*	*Corrected final temp.*
0 to 1	θ_0	θ_1	$\frac{(\theta_0 + \theta_1)}{2}$	x_1	x_1	$\theta_1 + x_1$
1 to 2	θ_1	θ_2	$\frac{(\theta_1 + \theta_2)}{2}$	x_2	$x_1 + x_2$	$\theta_2 + x_1 + x_2$
2 to 3	θ_2	θ_3	$\frac{(\theta_2 + \theta_3)}{2}$	x_3	$x_1 + x_2 + x_3$	$\theta_3 + x_1 + x_2 + x_3$

For the first interval, x_1 represents the amount by which the temperature at the end of the interval *viz.* θ_1 will be less than what it would have been in the absence of loss by conduction, radiation, etc. Hence the corrected final temperature for this interval is $\theta_1 + x_1$.

For the second interval, the rate of cooling is x_2 and the correction to be applied is $(x_1 + x_2)$ since θ_2 the temperature at the end of this interval will be less by this amount than what it would have been, had there been no loss during the first two intervals. The corrected temperature at the end of this second interval is therefore $\theta_2 + x_1 + x_2$.

Similarly the final corrected temperature at the end of the third interval is $\theta_3 + x_1 + x_2 + x_3$ and so on.

The values in the last column at a certain stage become practically constant giving the maximum temperature the calorimeter and contents would have attained if there had been no loss of heat.

Specific heat at high and low temperatures. For determining the specific heat at *high temperatures* by the method of mixtures, the solid is heated in an electric furnace. It is suspended inside the furnace by means of a loop of platinum wire and is dropped into the calorimeter by a mechanical device. The rise in temperature of the calorimeter and contents is measured by a resistance thermometer. For temperatures above 400°C, water is replaced by aniline as calorimetric liquid. For the study of specific heat at *low temperatures*, the solid is cooled in a vacuum vessel surrounded by liquid air, before being dropped into the calorimeter.

The copper block calorimeter (Fig. 50) was first designed by Nernst, Lindemann and Koref, to overcome the follwing limitations of using water as calorimetric liquid :—The range of water is very small ; also its specific heat being large, the rise of temperature will be small, which will increase the percentage of error ; further there is a risk of some amount of water being lost by evaporation.

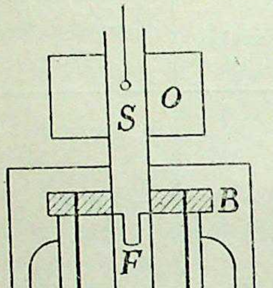


Fig. 50. Copper block calorimeter.

The copper block calorimeter consists of a thick copper block C cemented to the inside of a Dewar flask D with Wood's alloy. This block plays the same part as water in the ordinary calorimeter. The calorimeter is enclosed in an outer vessel to prevent still further any loss of heat.

The solid, S, whose specific heat is to be measured, is heated in an electric furnace O to any high temperature desired. It is then dropped into the copper block through a glass tube P. Actually the specimen in falling first reaches a small copper vessel F, which is held in position by means of a spring and piece of stiff paper that is torn away as soon as the solid falls on it. The vessel F serves the purpose of protecting the falling specimen from air currents ; further it has two projections soldered to it, which enable it and the specimen to be easily removed from C, in which they stick after the fall. As soon as the solid is thus carefully dropped into C, a lid V which closes the mouth of C is quickly released by an electrical contrivance.

The change in temperature of the calorimeter is read by means of a thermocouple TT, one junction of which is inside the copper block C, while the other in the block B, which is maintained throughout at a constant temperature. The copper block C, on account of its good conductivity, renders the temperature uniform throughout the mass in a short time.

Magnus, using the copper block calorimeter determined the specific heat of Pt and other metals up to 900°C. Jaeger and his collaborators employed the same technique to measure the specific heats of W, Pt, Os, Rh, Ir, etc., up to about 1600°C with a high degree of accuracy.

2. Electrical method. Gaede was the first to use this method for determining the specific heat of solids. Later, E.H. Griffiths and E. Griffiths perfected the technique and measured the specific heats of many metals in the range − 160°C to + 100°C. The solid, S, whose specific heat is to be found, is itself used as the calorimeter, round which a heater coil CC is wound. It is enclosed in vacuum flask V to minimise errors arising from conduction and radiation. The heater coil itself is made use of to measure the temperature as a resistance thermometer.

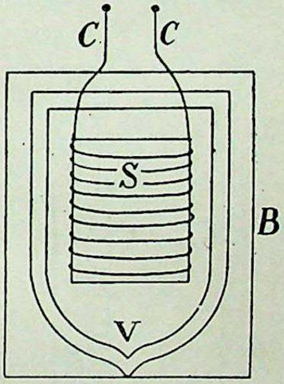


Fig. 51. Electrical method.

The solid is first cooled below the desired temperature, as measured by the resistance of the heater coil. Then a known current I is passed under a known potential difference E for a given time *t*. The final temperature is determined by measuring the final resistance of the heater coil.

The calorimeter is enclosed in a constant temperature bath B, which consists of a long spiral, through which air cooled to any required temperature and kept constant to 1/100th of a degree is circulated. This delicate control of temperature and hence the accurately known constancy of the bath are the chief advantages of this technique.

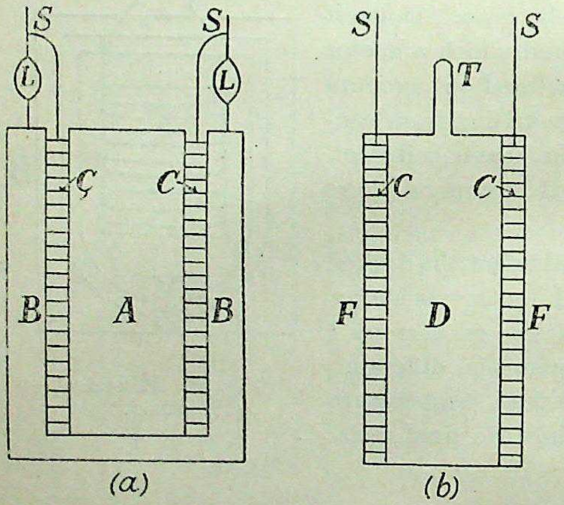
Correction for radiation is also applied. The specific heat of the solid is determined by using the relation

$$EIt = Jms\,(\theta + \delta\theta)$$

where $\delta\theta$ is the estimated radiation correction, J the mechanical equivalent of heat, m the mass of the solid, s its specific heat and θ the difference between the final and initial temperatures.

Nernst vacuum calorimeter. Nernst and Lindemann have used the electrical method for measuring the specific heat of solids at *very low* temperatures. There are two chief difficulties to be overcome in this type of research :—(*i*) Radiation correction, which is in the present case gain, not loss, of heat, becomes considerable at low temperatures. (*ii*) In the study of variation of specific heat with temperature, there is no advantage in allowing the calorimeter to rise much in temperature ; the change in temperature should be kept small, for which the electrical method, where the temperature can be kept under complete control, is best suited.

Nernst has devised a special type of calorimeter, known as the *Nernst vacuum calorimeter* which is most suited for low temperature work. It is of two types, one for good conductors and the other for bad conductors, illustrated in Fig. 52. For good conducting solids, the calorimeter has the form shown in (*a*). The solid is taken as a cylinder A, on which a coil CC of pure platinum wire is wound to serve both as electric heater and resistance thermometer. The coil is insulated from the cylinder by means of a thin sheet of paraffined paper. The cylinder and coil thus prepared is fitted inside a hollow cylinder B of the same material as A and the narrow inter-space is filled with paraffin wax to insulate B also from the coil. The calorimeter is suspended by the leads SS of the platinum coil, which are insulated from the outer cylinder by the non-conducting loops LL.



(*a*) (*b*)

Fig. 52. Nernst vacuum calorimeter.

For solids which are bad conductors, the calorimeter, shown in (*b*), consists of a hollow cylindrical silver vessel D on which the coil of platinum wire is wound. This is covered with silver foil, soldered at the bottom to the vessel, which not only prevents loss of heat from the coil to the surroundings but also helps in distributing the heat uniformly to the vessel. The solid to be experimented upon is placed inside the vessel which is then closed with the lid. The silver of the vessel on account of its high conductivity keeps the distribution of heat even. The narrow tube T in the lid is closed with a drop of solder in order to prevent the air inside D from escaping. It is essential that air should be present inside the vessel to help in the distribution of heat from the walls of the vessel to the solid inside it. The calorimeter is suspended by the leads of the platinum coil.

The calorimeter C thus constructed is mounted in a suitable glass bulb B which can be evacuated, as shown in Fig. 53. The glass bulb with the calorimeter in it is brought down to any required low temperature by immersing it in liquid air or liquid hydrogen and circulating in the bulb hydrogen which is a good conductor of heat. The bulb is then completely evacuated and sealed, so that loss of the heat through conduction and radiation is almost entirely eliminated, as indicated by the fact that no change in temperature can be observed even after an interval of several hours.

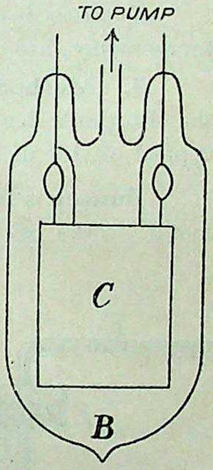


Fig. 53.

To determine the specific heat at a given low temperature, a current is passed through the platinum coil which is connected in series to a battery, a variable resistance and a precision ammeter; a voltmeter connected in parallel indicates the potential difference across the coil. Allowing the current to flow for a given time say t secs., the voltage across the coil is maintained at a constant value E by adjusting the variable resistance, and the initial and final values of current I_1 and I_2 are noted. From the known values of E, I_1 and I_2, the initial and final resistances R_1 and R_2 of the coil are readily determined, since

$$R_1 = \frac{E}{I_1} \text{ and } R_2 = \frac{E}{I_2}$$

If the resistance of the coil at various temperatures has been previously measured, with the values of R_1 and R_2 now obtained, the rise in temperature $\delta\theta$, which is usually about 1°C, can be found.

Since the electrical energy supplied is EIt, when I is the average value of the current, the specific heat of the solid forming the calorimeter at the low temperature chosen is given by the relation

$$EIt = Jms\delta\theta + h$$

where h is the heat loss which will evidently be very small and can be estimated by observing the rate of cooling before and after the experiment.

In the case of bad conductors, allowance is made for the thermal capacity of the silver vessel and foil.

It may be noted that (*i*) the second type of calorimeter meant for bad conductors can be used also for the determination of the specific heat of liquids and gases and (*ii*) both the types, though designed for low temperature work, can be used also at ordinary temperatures.

The results obtained by Nernst and Lindemann, working at low temperature, are of great theoretical importance, as we shall see.

3. Method depending on latent heats. We shall describe the Bunsen's ice calorimeter and the Joly's steam calorimeter as typical of this method of determining the specific heat of solids.

Bunsen's ice calorimeter. The *principle* on which this calorimeter works is that the quantity of heat lost by the hot body is determined by the mass of ice melted, which itself is estimated by the proportionate change in volume that occurs during the melting. The apparatus, shown in Fig. 54, consists of a test-tube A fused into a wider glass bulb B provided with a glass tube CD at its bottom. A wide cistern E is fitted to the free end of CD. A graduated capillary tube F bent at a right angle near one of its ends is passed through a cork which covers the cistern and arranged so that its short vertical arm is well inside the cistern, while its long arm is kept horizontal. Before fitting the capillary tube, air-free water is first poured into the cistern and then mercury, the former nearly filling the bulb B while the latter the remaining space of the bulb, the glass tube CD and the cistern, so that, with F in position, there is a thread of mercury up to a certain graduation in the horizon-

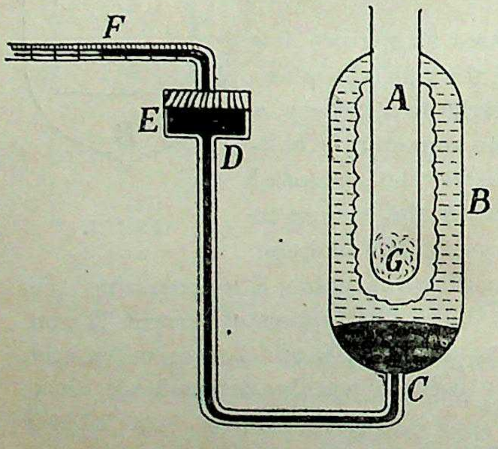


Fig. 54. Bunsen's ice calorimeter.

tal part of F. Some glass wool G is placed at the bottom of A to prevent breakage when the solid is dropped in. The water inside B is cooled by passing a stream of ice-cooled alcohol or ether into the test-tube A, so that a thick layer of ice is formed round the outer surface of A.

To perform the experiment, the scale on F is first *calibrated* as follows :—

A known mass m of water at a definite temperature θ is introduced into A. Due to the heat communicated by the water, some ice in the layer surrounding A melts causing a contraction in volume. This, in turn, makes the mercury level in B to rise and the thread of mercury in F recedes, say through x divisions of scale. If q calories be the quantity of heat required to cause the recession of the mercury thread by 1 scale division, then

$$m\theta = xq \text{ or } q = m\theta/x \text{ calories.}$$

To find the specific heat of a solid, the latter is heated to a known temperature t and dropped into A. The consequent recession of the mercury thread in F is noted. Let it be y divisions. If M be the mass of solid and s its specific heat, we have

$$\mathrm{M}st = yq$$

$$s = \frac{y}{\mathrm{M}t} \cdot q = \frac{m\theta}{\mathrm{M}t} \cdot \frac{y}{x}$$

Since all the quantities on the right hand side of this relation are known, the specific heat s is readily calculated.

The *advantages* of this method are :—

1. It is independent of the value of the latent heat of fusion L, since it takes into account only the contraction in volume during fusion.

2. Radiation error is eliminated since the calorimeter is always packed in a layer of ice.

3. Amounts of heat up to 0·01 calorie can be estimated easily.

4. The specific heat of rare metals which can be obtained only in small amounts can be determined.

The *accuracy* of the method depends chiefly on the purity of water contained in the bulb B ; hence it is limited by the fact that a given specimen of water can freeze into ice of different densities ; but the error due to this cause cannot exceed about 1 in 1000.

The apparatus can be used in the case of liquids also.

Joly's steam calorimeter. The *principle* involved in this method is that heat necessary to raise a body from the room temperature to that of steam is measured by the mass of steam condensed into water at the same temperature to supply that heat.

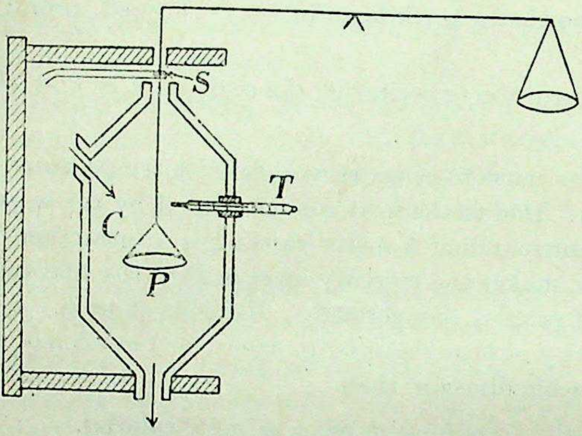


Fig. 55. Joly's steam calorimeter.

The apparatus (Fig. 55) consists of a specially designed metal chamber C with suitable holes for letting steam in and out and for inserting a thermometer T. The top and bottom portions of the chamber are conical shaped in order that the steam condensed on the inner walls of the chamber may be drained away quickly. The chamber is covered on the outside with black cloth to eliminate radiation. Inside this chamber hangs freely a light pan P suspended from one of the arms of a sensitive balance, by means of a very fine wire. In order to prevent steam from condensing on the suspension wire and blocking the narrow hole through which the wire leaves the chamber, which will render accurate weighing difficult due to surface tension effect, a thin spiral of platinum wire S carrying a current is arranged round the wire above the hole, so that the heat developed in the spiral just prevents condensation. It is also essential that steam condensed on the walls of the chamber does not fall into the pan.

First of all, the *thermal capacity of the pan* P in the chamber is determined as follows: P is carefully counterpoised by placing weights in the other pan, and the initial temperature θ_1 of the chamber is noted. Steam at full pressure is suddenly let in, which after circulating in the chamber escapes through the outlet at the bottom. A rapid flow of steam through the chamber is necessary chiefly at the beginning, in order to prevent partial condensation of steam due to radiation to the cold air and walls of the chamber. Steam condenses on the pan P and weights are added on the other pan to maintain balance. After about five minutes, when P ceases to increase in weight the temperature of steam θ_2 is noted. In the final stage of balancing, the steam supply is slowed down in order to avoid steam draught on P, which would prevent accurate weighing. The difference between the two weights used for counterpoising at the start and finish gives the weight of steam condensed on the pan P alone Let it be w grams.

Next, the solid, whose specific heat is to be determined, is placed on P, after drying the latter carefully. The operations described above are repeated and the weight W grams of steam condensed on both the solid and pan determined.

If m is the weight of the solid, s its specific heat, and L the latent heat of steam,

$$ms(\theta_2 - \theta_1) = (W - w) L$$

from which s can be calculated, assuming the value of L.

The *advantages* of this method are : 1. It can be used for solids of even small mass, so that the specific heat of rare substances can be determined, provided a sensitive balance is used. 2. It is equally applicable to powders, liquids and gases. In the case of powders and liquids, glass or metal containers are used and their thermal capacity taken into account. For gases, an improved form of apparatus is used as we shall see later.

To obtain great *accuracy* of results, correction is to be made for the fact that the two weighings are made one in air at θ_1°C and the other in steam at θ_2°C, which introduces a difference in buoyancy. Also all the weighings must be reduced to vacuum, before calculating the weight of steam condensed.

It is of interest to note that Dewar used a *liquid air calorimeter* to estimate the specific heat of solids. The solid is kept in a constant temperature bath, say of melting ice, and then it is dropped into liquid air. Due to the heat imparted by the solid, part of the liquid air evaporates. The air thus obtained as a result of evaporation is collected in a manometer tube inverted over a trough of water. The volume of the air can then be estimated. Let it be v_0. If ρ_0 is the density of air at that temperature, $v_0\rho_0$ is the mass of the liquid air that has evaporated. Knowing the latent heat of vaporisation of the liquid air, the specific heat of the solid, whose mass is m, can be calculated from the relation

$$ms(\theta_1 - \theta_2) = v_0\rho_0 \, L$$

where θ_1 is the initial temperature of the solid, θ_2 its final temperature, *i.e.*, that of the liquid air and L the latent heat of liquid air. Using liquid oxygen and liquid hydrogen, the specific heat can be measured down to very low temperatures.

Results. The results obtained from the study of the specific heat of solids at different temperatures, chiefly very high and very low, have led to conclusions of far-reaching importance.

(*a*) **Dulong and Petit's law.** In 1819, Dulong and Petit, as a result of their investigations on the specific heats of elements in the solid state, were able to enunciate a law, which is named after them, *viz.*, *the product of the atomic weight and specific heat, i.e., the atomic heat is constant for elements in the solid state.* This means that atoms of different elements have the same capacity for heat.

Regnault, from his own researches on the specific heats of a great number of the common solid elements, measured at ordinary temperatures (*i.e.*, far below their melting points) obtained the following results which confirmed Dulong and Petit's law.

Element	*Atomic weight*	*Specific heat*	*Atomic heat*
Lithium	7·0	0·9408	6·59
Boron	11·0	0·2500	2·75
Carbon	12·0	0·1470	1·76
Sodium	23·0	0·2934	6·75
Magnesium	24·3	0 2470	6·00
Aluminium	27·0	0·2143	6·79
Silicon	28·3	0·1760	4·98
Phosphorus	31·0	0·2120	6·57
Sulphur	32·0	0·2026	6·48
Potassium	39·0	0·1660	6·48
Calcium	40·1	0·1489	5·98
Iron	55·8	0·1138	6·35
Nickel	58·7	0·1080	6·40
Copper	63·6	0·0952	6·05
Zinc	65·4	0·0956	6·28
Silver	107·9	0·0570	6·16
Cadmium	112·4	0·0557	6·26
Tin	118·0	0·0548	6·46
Platinum	195·2	0·0324	6·30
Gold	197·2	0·0324	6·35
Mercury	200·6	0·3019	6·38
Lead	207·2	0·0314	6·51

It is seen that, with the exception of three elements, boron, carbon and silicon, in all the other cases, as the atomic weight increases the specific heat decreases, making the atomic heat more or less constant. Regnault found the mean value of the constant to be 6·4 with extremes of 6·8 and 5·8. A more accurate value of the constant can be obtained theoretically from the kinetic theory of matter, where considering the specific heat at constant volume it will be shown to be equal to 5·96. The specific heat at constant pressure, the quantity measured experimentally, being slightly greater than that at constant volume, its value should be slightly greater than 6. Hence it is concluded that the atomic heat at constant volume of all elements in the solid state is about the same and equal to 6·0 calories nearly per gram-atom per °C, which is Dulong and Petit's law. This law was used in former times to determine the atomic weights of rare elements.

Woestyn extended Dulong and Petit's law to the case of metallic compounds and stated that the *molecular heat of a compound might be considered as the sum of the atomic heats of its constituents.* If this statement is true, the specific heat of a compound can be determined, from the known specific heats of its constituents. Newmann, however, found Woestyn's law to have a limited application, *i.e.*, only in the case of *compounds of similar composition* and hence enunciated the law : *the product of the specific heat and the molecular weight of compounds that are similarly constituted, is nearly a constant*, as illustrated in the following table :—

Compound	*Molecular weight*	*Specific heat*	*Molecular heat*
NaCl	58·5	0·214	12·5
KCl	74·5	0·173	12·9
AgCl	143·4	0·091	13·0
Fe_2O_3	159·8	0·1700	27·2
As_2O_3	197·8	0·1277	25·3
Sb_2O_3	287·8	0·0901	25·9

Newmann's law has been used in finding the molecular heats of certain substances.

(*b*) **Variation of specific heat with temperature.** We have seen above that the elements boron, carbon and silicon do not seem to fall under Dulong and Petit's law, their atomic heats differing greatly from 6·0. But measuring the specific heats of these elements at high temperatures, 500°C and above, it can be shown that their atomic heats also reach the value given by Dulong and Petit's law. Hence consideration of the variation of specific heat with temperature must be taken into account in the enunciation of a perfect law about atomic heats. The empirical deduction of Dulong and Petit is only a first approximation to the truth and cannot explain all the facts, since it does not take into account the variation of specific heat with temperature. This is also the reason why the atomic heats are not strictly constant in the several cases cited above. Kinetic theory of matter, which justifies Dulong and Petit's law, predicts at the same time that the atomic heat should be independent of temperature, as we shall see later. This is contrary to the observed variation of specific heat with temperature.

The specific heat of solids, in general, increases with rise of temperature, although the increase is very small at temperatures far removed from the melting point. Some metals, like lead, tin and platinum, exhibit only very small variations of specific heat with temperature, platinum the least. A few substances like carbon, boron and silicon show very large variations of specific heat with temperature. Thus, for instance, carbon, in the form of diamond, at 200°C has a specific heat which is nearly three times its value at 0°C, at 300°C nearly four times the value at 0°C, and reaches a fairly constant value only above 600°C. It has also been shown that diamond does not reach the theoretical value of atomic heat below a temperature of 980°C. In the case of silicon, the specific heat increases rapidly with rise of temperature, reaching a fairly constant value above 200°C. It may be noted that elements which occur in different allotropic forms have different specific heats even at ordinary temperatures. Thus the specific heat of carbon in the form of diamond is 0·1469, wood charcoal 0·2415 and graphite 0·2148. Calcium carbonate has specific heats of 0·2085 in the form of iceland spar, 0·2148 as chalk and 0·2158 as marble.

Measurement of specific heats made by Nernst and his collaborators down to temperatures as low as that of liquid hydrogen and below show that below a certain temperature characteristic of each element, the specific heat decreases rapidly with temperature, tending ultimately towards a value zero at the absolute zero for all elements. The following results obtained in the case of silver illustrate very well the above statement.

Atomic heat of silver at different low temperatures :

Temperature in °K	Atomic heat
205·3	5·605
144·4	5·373
103·1	4·797
74·6	4·039
55·9	3·186
36·2	1·694
20·0	0·3995
10·0	0·0475
5·0	0·0051
1·35	0·000254

These results, when represented graphically, give a curve of the form shown in Fig. 56. It is seen that the atomic heat tends to the value of 6·0 at high temperatures and to the value zero at absolute zero, decreasing rapidly below a certain temperature, characteristic of the element. Similar curves are obtained for other elements. A satisfactory explanation of such variations in specific heat and the consequent deviations from Dulong and Petit's law can now be had on the basis of the modern quantum theory.

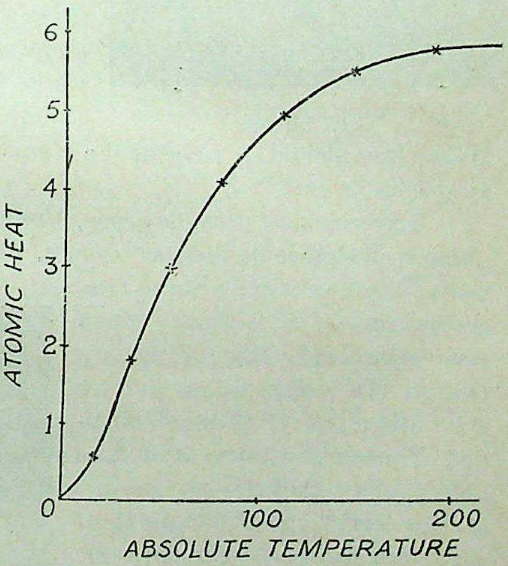
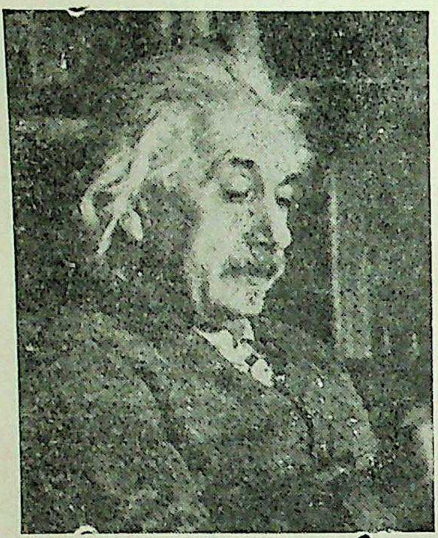


Fig. 56.

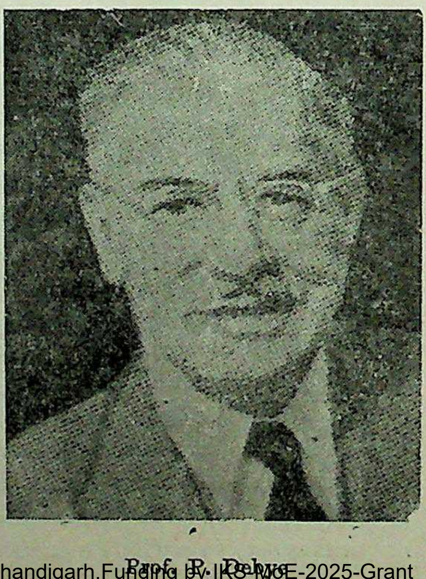
The quantum theory of specific heats. The quantum theory was first suggested by Max Planck in 1901 to account for the fundamental laws of radiation, which the classical theories had completely failed to explain. The revolutionary feature of Planck's theory is that the energy of an oscillating system varies not in a continuous fashion permitting all possible values, as conceived by the classical theory, but in a *discontinuous manner, in a discrete quantified form, as integral multiples of an* *elementary quantum of energy hν*, where h is a constant of proportionality, now known as *Planck's constant*, and ν the frequency of oscillation.



Prof. Einstein

In 1906, Einstein applied the quantum theory to the problem of atomic heats of solid elements with remarkable success and was able to show that (*i*) the atomic heat should increase with temperature and tend asymptotically to the value demanded by Dulong and Petit's law, which is, therefore, a limiting law valid only when the temperature is sufficiently high, although for many substances the ordinary temperature satisfies this condition, while boron, carbon and silicon require high temperatures ; (*ii*) the atomic heat should decrease as the temperature falls, tending to zero at absolute zero.

Experimental data, however, showed that, in the case of a number of elements, such as copper, aluminium, etc., the atomic heats at low temperatures decreased much more slowly than was predicted by Einstein's theory. In order to account for this discrepancy, Debye modified Einstein's theory and was able to show that (*i*) the nature of the variation of atomic heat with temperature will be the same for all elements, *i.e.*, the graphs of atomic heat *vs.* absolute temperature of all elements will coincide if the temperature scale is suitably adjusted ; analytically expressed $A = f(\theta/T)$ where A is the atomic heat of an element at the absolute tem-



Prof. P. Debye

perature T, θ = a parameter known as *Debye's temperature* which is a constant for a given element, but varies from element to element and $f(\theta/T)$ which is the same for all elements, is zero at absolute zero and tends to 6·0 at high temperature ; (*ii*) the specific heat of a body at low temperatures is proportional to the third power of the absolute temperature, known as *Debye's T^3 law*, which has also been experimentally verified.

Attempts have been made to introduce greater precision in Debye's theory and extend it to substances other than simple chemical elements. Thus Born and Karmann have developed the *lattice theory of atomic heats* for the most general case of crystals and chemical compounds, which shows better agreement with observations than Debye's theory.

Sir C. V. Raman, as a result of his investigation on X-ray reflections from crystals, has criticised rather adversely Debye's theory, and has tried to show that the so-called Debye temperature is purely arbitrary, having no great physical significance, except perhaps at the lowest temperatures. A more detailed treatment of the subject is beyond the scope of this book.

SPECIFIC HEAT OF LIQUIDS

All the methods employed for solids can also be used for liquids with the necessary changes. Thus in the *method of mixtures*, if the liquid whose specific heat is required is placed in the calorimeter instead of water and a solid of known specific heat that does not enter into chemical combination with the liquid is heated and mixed with the liquid in the usual way, the specific heat of the liquid can be calculated from the data of the experiment. Another method is to enclose the liquid in a small thin bulb made preferably of a good conductor and use it just as in the case of a solid, making the necessary correction for the thermal capacity of the bulb. Similarly the two *latent heat methods*, *viz.*, the Bunsen's ice calorimeter and Joly's steam calorimeter can also be used to determine the specific heat of liquid as already indicated. But the *method of cooling* and the *electrical method* are the two which are ordinarily used as most suited for liquids.

1. Method of cooling. This method is based on the supposition that when a body is allowed to cool in an enclosure the heat dQ lost by it in time dt through radiation alone is given by the relation

$$dQ = K \, . \, f\,(\theta) \, . \, dt$$

as already indicated.

If the body cools through $d\theta$ in the time dt,

$$dQ = m\,s\,d\theta$$

where m is the mass of the body and s its specific heat.

$$\therefore \qquad m\,s\,d\theta = K\,f\,(\theta)\,dt$$

The time t taken by the body to cool from $\theta_1°$ to $\theta_2°$ is given by the relation

$$\int_0^t dt = \int_{\theta_2}^{\theta_1} \frac{msd\theta}{Kf(\theta)}$$

$$t = \frac{ms}{K}\left[F(\theta_1) - F(\theta_2)\right] \qquad \dots (1)$$

where $F(\theta)$ is the function obtained by integration of $\dfrac{d\theta}{f(\theta)}$.

Similarly, the time t' taken by another body of mass m' and specific heat s' to cool through the same range of temperature in the same enclosure is given by

$$t' = \frac{m's'}{K'}\left[F(\theta_1) - F(\theta_2)\right] \qquad \dots (2)$$

From (1) and (2), we get

$$\frac{t}{t'} = \frac{ms}{m's'} \cdot \frac{K'}{K}$$

If the surface area and the radiating power of the two bodies are the same, then $K = K'$, and $\dfrac{t}{t'} = \dfrac{ms}{m's'}$

Taking into account the water equivalent w of the containing vessel,

$$\frac{t}{t'} = \frac{ms + w}{m's' + w}$$

Of the two bodies considered, if one is water, $s = 1$, the specific heat s' of the other, a liquid, can be determined from a knowledge of t, t', m and m'.

To determine the specific heat of a liquid by this method, a convenient means usually adopted in the laboratory is the following :—

A calorimeter spherical in shape with a small orifice just wide enough to insert a thermometer is used. The spherical shape helps to keep the nature and extent of the radiating surface constant while the narrow orifice is to prevent loss of heat by evaporation since the experiment is based on the study of loss of heat by radiation alone.

The calorimeter is weighed dry and empty. It is then filled with hot water at about 80°C, and suspended from a stand by means of a thread so as to avoid all conduction effects and placed in a draught-free enclosure. A thermometer is inserted in the water to note the temperature. As the calorimeter and contents cool steadily by radiation, time is recorded with a stop-watch at every one or two degree fall of temperature, until the temperature is reduced to, say 50°C. The calorimeter with the water is weighed, after removing the thermometer and allowing some time for the calorimeter to become sufficiently cool for weighing.

The water is poured out completely and the calorimeter is dried and then filled with the liquid (whose specific heat is to be determined) at about 80°C. The calorimeter is again allowed to cool under the same conditions as in the previous case and observations are made as before, noting the time for the same ranges of temperature. At the end, the calorimeter with the liquid is weighed.

Let the time taken for the temperature to fall through a certain range, say from 75°C to 71°C be t_1 in the case of water and t_2 in the case of the liquid. Let m_1 be the mass of water filling the calorimeter, m_2 the mass of liquid filling the same, w the water equivalent of the calorimeter and s the specific heat of the liquid.

Heat lost by the calorimeter with water in cooling from 75°C to 71°C. $= (m_1 + w) \times 4$ calories.

$\therefore$ Rate of loss of heat in the case of water for the range considered $= \dfrac{(m_1 + w)\,4}{t_1}$ cals./sec.

Similarly, rate of loss of heat in the case of the liquid for the same range $= \dfrac{(m_2 s + w)\,4}{t_2}$ cals./sec.

$$\text{Since} \quad \frac{(m_1 + w)\,4}{t_1} = \frac{(m_2 s + w)\,4}{t_2},$$

$$\therefore \; s = \frac{1}{m_2}\left[\frac{t_2}{t_1}(m_1 + w) - w\right]$$

Since all the quantities on the right hand side of this equation are known, s can be calculated. Considering, in a similar manner, other temperature ranges, s can be calculated for each of them, so that the specific heat of the liquid may be obtained as the average of several values.

Graphical method. From the data obtained, the specific heat can be determined also by a graphical method as follows. Cooling curves for water and the liquid are drawn on the same graph sheet, taking temperature along the Y-axis and time along the X-axis, as shown in Fig. 57. At any particular temperature (indicated by the dotted line) tangents to the two curves are drawn. If these are inclined at angles α and β to the X-axis, tan α and tan β give the rate of fall of temperature in the two cases at the temperature chosen. The fact that the rate of cooling should be the same at the same temperature gives the relation.

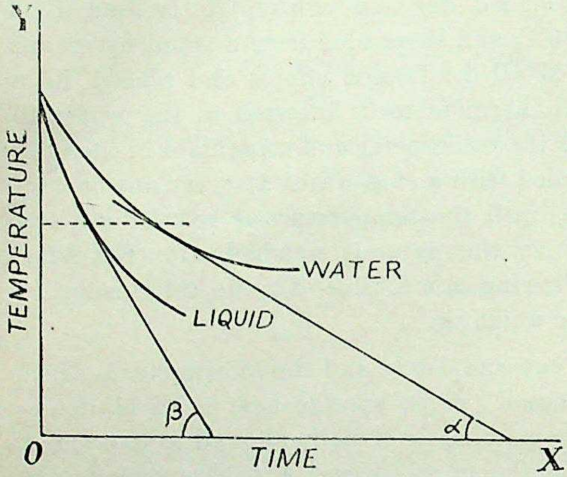


Fig. 57.

$$(m_1 + w) \tan\alpha = (m_2 s + w) \tan\beta,$$

from which s can be calculated.

The mean of the values of tan α/tan β obtained by drawing tangents at different temperatures is used in the calculation.

The *advantage* of this method is that it involves no transference or mixture and no cooling correction. But it is *not capable of giving results of any great accuracy*. The reason for this is that the measurement is based on the assumption that the rate of loss of heat is the same in the two cases. Hence any variation in the conditions under which the two cases are studied or uncertainty in the rate of loss of heat produces its full effect in the result. To minimise these errors, a large surface is used and the surface is blackened so as to increase the loss of heat by radiation compared to the loss by conduction or convection.

2. Electrical method. With liquids this method is applied in two distinct forms, the one known as *Joule's method* depending on the observation of rise of temperature and the other *Callendar and Barnes' continuous flow method* devised in order to have no change of temperature in any part of the apparatus.

(*i*) **Joule's method.** A thinly insulated heater coil H is suspended in a calorimeter C covered with an ebonite lid L ; the ends of the coil are soldered to two thick copper wires which connect the coil with two binding screws on the top of the lid. A sensitive thermometer T and a stirrer S can be introduced into the calorimeter through holes in the lid. The calorimeter is supported within a non-conducting box to prevent loss of heat by conduction and radiation as much as possible. The heater coil is connected in series with a battery B, an ammeter A, a rheostat R and a tap-key K. A voltmeter V is connected in parallel with the heater coil to measure the p.d. between its ends (Fig. 58).

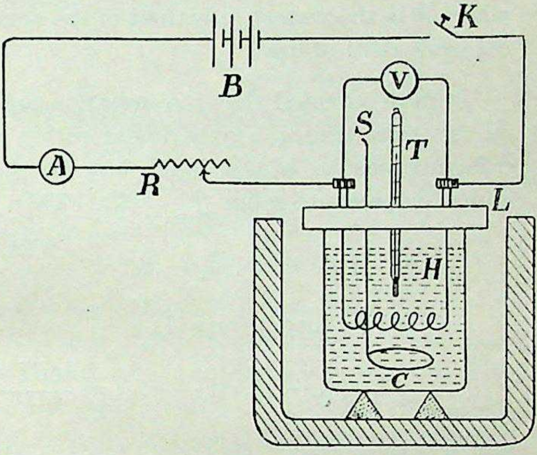


Fig. 58. Joule's method.

The liquid, whose specific heat is to be determined, is poured into the calorimeter until the coil is completely immersed in it. The mass m of the liquid taken is known by weighing the calorimeter first empty and then with the liquid.

Closing the electric circuit, the rheostat is quickly adjusted in order to have a pretty slow rate of rise of temperature (about ½°C per min.) in the calorimeter. A current of about one ampere is ordinarily found convenient. The current is cut off and after stirring well the contents of the calorimeter, its initial temperature is noted accurately. Let it be θ_1. The tap-key is closed and current allowed to pass through the coil for a known time t, until there is a rise of temperature of about 5°C ; the key is then released. During the time the current flows through the coil, the ammeter and voltmeter readings are taken every minute and the averages taken if there is any variation. Let them be I amperes and E volts.

Since the heating takes place for an appreciable time, accurate radiation correction must be applied. Let θ_2 be the final corrected temperature.

The specific heat s of the liquid can then be calculated from the relation

$$(ms + w)(\theta_2 - \theta_1) = \mathrm{EI}t/\mathrm{J} \qquad \dots (1)$$

where w is the water equivalent of the calorimeter and J the mechanical equivalent of heat.

It may be noted that the radiation correction is usually eliminated by repeating the experiment with a p.d. E′ and current I′ for a different mass m' of the liquid, but for the same time t, over the same temperature range $(\theta_2 - \theta_1)$. Then

$$(m's + w)(\theta_2 - \theta_1) = \frac{\mathrm{E'I'}t}{\mathrm{J}} \qquad \dots (2)$$

Subtracting (2) from (1)

$$s(m - m')(\theta_2 - \theta_1) = \frac{(\mathrm{EI} - \mathrm{E'I'})\,t}{\mathrm{J}}$$

$$\therefore \qquad s = \frac{(\mathrm{EI} - \mathrm{E'I'})t}{\mathrm{J}(m - m')(\theta_2 - \theta_1)}$$

The water equivalent of the calorimeter w is also eliminated by this device.

This method is ordinarily used in the laboratory and gives fairly accurate results. Jaeger and Steinwehr have employed it in their researches on the variation of specific heat of water with temperature and with an improved form of apparatus, have been able to get results to an accuracy of 1 in 10,000. The main features of their technique are : A large mass of water, 50 kgms., is used in a suitably big copper calorimeter arranged inside a constant temperature bath. The heater coil is made of constantan, of 8 ohms resistance, which gives a rise of temperature of about 1·5°C when a current of 10 amperes is passed. The temperature rise of the calorimeter and contents is accurately measured by a resistance thermometer ; big electrically driven stirrers are used in the calorimeter.

(*ii*) **Callendar and Barnes' continuous flow method.** The apparatus consists of a narrow glass or quartz tube G, inside which a fine platinum wire W in the form of a spiral is mounted, with its ends fixed to thick copper tubes CC (Fig. 59). The liquid whose specific heat is to be determined is made to flow continuously through G at a steady rate and is heated as it flows by passing an electric current through W by means of the leads LL, attached to the copper tubes

CC. The spiral form of W helps in the thorough mixing of the liquid as it flows along the tube.

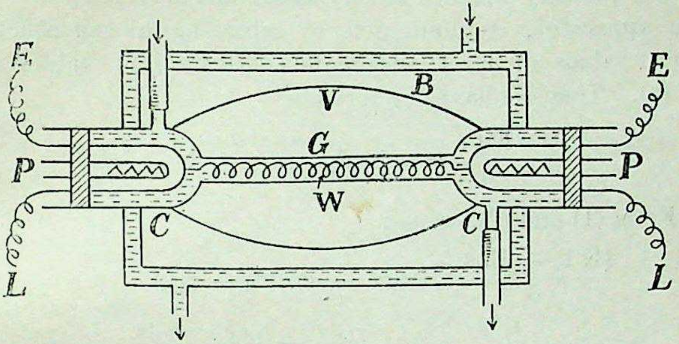


Fig. 59. Continuous flow method of Callendar and Barnes.

The temperatures of the inflowing and outflowing liquid are measured by a pair of platinum resistance thermometers PP, with their bulbs inserted in the thick copper tubes CC. These tubes, on account of the good conductivity of copper, keep the bulbs of the thermometers at the temperatures of the adjacent liquid, while on account of their low resistance, develop only a negligible amount of heat by the current near the thermometer. The leads EE, attached also to the copper tubes, are used for measuring the potential difference between the ends of W. The tube G is enclosed in a vacuum jacket V to reduce radiation correction to a minimum ; V, in its turn, is surrounded by a cold water constant temperature bath B.

When sufficient time has been allowed for the apparatus to attain a steady state, the platinum resistance thermometers, connected suitably to a Callendar and Griffiths' bridge, are read and the temperature θ_1 of the liquid at entry into G and θ_2 at exit are estimated to an accuracy of 0·001°C. The mass of liquid m flowing through G for a given time t is determined accurately using a sensitive balance, the time being reckoned accurate to 0 01 sec., with an electric chronograph. The steady potential difference across the heater coil is measured with a sensitive potentiometer accurately calibrated in terms of the standard Clark cell. The same potentiometer is used to determine the heating current I by measuring the potential difference across a standard *one ohm* resistance in series with the heater coil.

To determine the specific heat of the liquid from the experimental data, we use the the relation

$$\frac{\mathrm{EI}t}{\mathrm{J}} = ms\,(\theta_2 - \theta_1) + \mathrm{R} \qquad \ldots (1)$$

where R is the heat lost by radiation during the time t.

The quantity R, which is very small due to the special design of the apparatus, is eliminated by repeating the experiment with different values of E, I and m but with the same values of t and $(\theta_2 - \theta_1)$. Then we have the relation

$$\frac{E'I't}{J} = m's\,(\theta_2 - \theta_1) + R \qquad \ldots (2)$$

From (1) and (2), we get

$$\frac{(E'I' - EI)t}{J} = s(m' - m)\,(\theta_2 - \theta_1)$$

$$\therefore \qquad s = \frac{(E'I' - EI)t}{J(m' - m)\,(\theta_2 - \theta_1)}$$

The great *advantage* of this method is that the temperature at every point of the apparatus is *steady* while measurements are being made. This means that :—

(*a*) the thermal capacity of the flow tube and contents is eliminated ;

(*b*) the rate of loss of heat is constant, so that it can be determined more accurately than if the temperature is varying ; or it may be eliminated, as indicated above.

(*c*) the temperature can be measured with great accuracy, without any danger of "lag".

Callendar used this method for finding the specific heat of mercury ; the heater coil in this case was dispensed with, since the continuously flowing mercury itself served as the conductor. Griffiths determined the specific heat of aniline over a range of 15 to 50°C.

Barnes employed the method to carry out successfully the very interesting research on the variation of specific heat of water with temperature, which is dealt with below.

It may be noted that this method offers itself as one of the most accurate means of determining the mechanical equivalent of heat, J.

3. Callendar's continuous flow and mixture method. In order to measure the specific heat of water at different temperatures with the greatest possible accuracy, Callendar devised a technique which is a most ingenious combination of the method of mixtures and the continuous flow method. The main features of his complicated apparatus are illustrated in Fig. 60. Air-free water is circulated at a steady rate through a closed system. From a *heater* maintained at a constant high temperature the stream of water flows into an *exchanger* with θ_4, the temperature of entry, about 100°C, and leaves it at a temperature θ_3, about 70°C. It then passes through a *cooler* maintained at a constant temperature where its temperature is reduced by a good amount. It returns to the exchanger, where its temperature θ_1, about 30°C, at entry is raised to θ_2, about 60°C, at exit. After passing through the exchanger the stream returns to the heater from which it emerges at the same temperature as before, to go through another cycle.

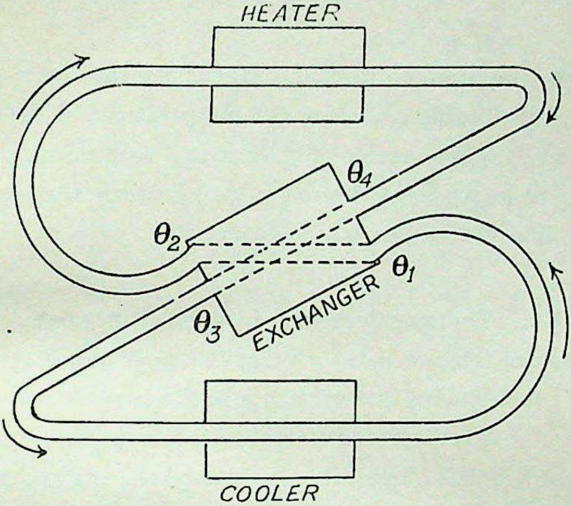


Fig. 60. Callendar's continuous mixture method.

In the exchanger, the hot stream gives heat to the cold stream, without any actual mixing taking place. The heat lost by the hot stream in any time is equal to the heat gained by the cold stream. The temperatures of the hot and cold streams at entry and at exit are measured to an accuracy of 0·001°C by platinum resistance thermometers. Radiation correction is reduced to a minimum by suitably arranging the circulating pipes inside the exchanger.

If m is the mass of water flowing past any section in the system in 1 sec., and if s_1 and s_3 are specific heats of water at the mean temperatures $\frac{\theta_1 + \theta_2}{2}$ and $\frac{\theta_3 + \theta_4}{2}$ respectively, we have

$$ms_3 (\theta_4 - \theta_3) = ms_1 (\theta_2 - \theta_1) + k$$

where k is the radiation correction. Hence the ratio of s_1 and s_3 can be found. By suitably adjusting the temperatures of the heater and cooler, the mean temperatures of the hot and cold streams in the exchanger can be kept at any desired value and thus the specific heat of water at different ranges can be measured.

Results. The specific heat of liquids, in general, increases with increase of temperature. One of the most important researches conducted is the detailed investigation of the variation of the specific heat of water with temperature, especially in the range 0°C to 100°C, on account of the unit chosen in calorimetry, the *calorie*, since if this unit varies with temperature, one must have an accurate knowledge of how it varies.

Variation of specific heat of water with temperature. The method of investigation is intimately connected with that used for the determination of the mechanical equivalent of heat. Rowland, in his mechanical method of measuring J, *i.e.*, developing heat by friction and communicating it to water, found that the value of J varied when water at different initial temperatures was used, which should be naturally attributed to changes in specific heat of water. Operating over a wide range of temperature, he was further able to conclude that the specific heat of water first decreased, reaching a minimum at 30°C and then increased gradually. Callendar and Barnes with their more refined electrical-continuous flow method, were able to confirm the findings of Rowland, however with a difference, *viz.*, the specific heat reaches a minimum value at about 37°C. Jaeger and Steinwehr also have studied the variation of specific heat of water with temperature with their elaborate technique mentioned earlier. The results obtained by Callendar and Barnes and Jaeger and Steinwehr are given in the following table :—

Temp. °C	*Specific heat of water*	
	Callendar and Barnes	*Jaeger and Steinwehr*
0	1·0093	(1·005)
5	1·0047	1·0029
10	1·0019	1·0013
15	1·0000	1·0000
20	0·9988	0·9990
25	0·9980	0·9983
30	0·9976	0·9979
35	0·9973	0·9978
40	0·9973	9·9981
45	0·9975	0·9987
50	0·9978	0·9996
60	0·9987	
70	1·0000	
80	1·0017	
90	1·0036	
100	1·0057	

It is seen that the specific heat reaches a minimum somewhere in the range 35° to 40°C, and its value is unity at 15°C, justifying the *choice of the '15°C calorie' as the thermal unit*, which has also the following other advantages, *viz.*, 15°C is the temperature to which other physical quantities are usually referred, and at which the mechanical equivalent of heat is known with great accuracy. But Callendar prefers the *20°C calorie i.e.*, one-tenth of the amount of heat required to raise 1 gram of water from 15°C to 25°C, on the plea that all calorimetric measurements use a finite range of temperature, that the range chosen is easily realised in practice and that the value of the 20°C calorie is very nearly the same as the mean calorie. The committee of the British Association proposed the value of the calorie at such a temperature as would make it equal to 4·2 Joules, but this, in Prof. Callendar's opinion, is merely an absolute unit and leaves the actual temperature uncertain. Thus, there is as yet no universal agreement over the thermal unit and hence it is still necessary to specify the particular unit used in really accurate measurements.

SPECIFIC HEAT OF GASES

The specific heat of a substance may be spoken of with definiteness only when the conditions under which the heating takes place are stated. If the specific heat is defined merely as the quantity of heat required to raise unit mass through 1°C, its value will depend not only on the nature of the substance, but also on the amount of external work done due to the expansion of the substance caused by the rise in temperature. In the case of solids and liquids, the change of volume and hence the external work done during change of temperature is negligibly small. But the same cannot be said of gases which can suffer big changes of both pressure and volume due to change in temperature. For this reason, the conditions under which the heating of a gas takes place must be stated when its specific heat is considered.

Two specific heats of a gas. It is customary to speak of two specific heats of a gas, *viz.*, *the specific heat at constant volume* (C_v) *i.e.*, the quantity of heat required to raise 1 gm. of the gas through 1°C, when its volume is kept constant and *the specific heat at constant pressure* (C_p) *i.e.*, the quantity of heat required to raise 1 gm. of the gas through 1°C, when its pressure is kept constant.

In the former case the whole heat supplied goes to increase the internal energy of the gas. In the latter case, since the gas is allowed to expand under constant pressure, the thermal equivalent of the external work done by the gas forms part of the total heat supplied. Hence *the specific heat at constant pressure is greater than the specific heat at constant volume* ($C_p > C_v$) by an amount equal to the thermal equivalent of the external work done by the gas. It may be noted that the specific heat at constant volume alone gives a true measure of the capacity of the body for heat.

Difference between the two specific heats. A relation for the difference between C_p and C_v in terms of the gas constant R may be obtained as follows :—

In an *ideal* gas, the molecules are outside the sphere of mutual attraction, so that when such a gas expands no internal work is done, but only external. Let us suppose that unit mass of the ideal gas is heated at constant pressure p so that its temperature increases by dT ; let the volume increase by dv due to the rise in temperature. The external work done by the gas in expanding $= pdv$ ergs $= \frac{p\,dv}{J}$ calories. Since the difference between C_p and C_v is equal to the thermal equivalent of the external work, both referred to dT,

$$(C_p - C_v)\,dT = \frac{p\,dv}{J} \qquad (1)$$

But $$pv = \text{R}T \text{ for an ideal gas}$$

Or $$p\,dv = \text{R}\,d\text{T}$$

Substituting this value of $p\,dv$ in (1)

$$(\text{C}_p - \text{C}_v)\,d\text{T} = \frac{\text{R}d\text{T}}{\text{J}}$$

Or $$\text{C}_p - \text{C}_v = \frac{\text{R}}{\text{J}} \qquad \dots (2)$$

If R is expressed in calories, or C_p and C_v in ergs, then, in either case

$$\text{C}_p - \text{C}_v = \text{R} \qquad \dots (3)$$

This relation, first derived by Mayer in his researches on the equivalence of heat and energy is strictly true only for perfect gases where no internal work is done, while it holds good approximately in the case of the permanent gases such as hydrogen, helium, etc., as was experimentally established by Gay-Lussac and Joule. The relation can be used to determine one of the two specific heats when the other one is known, assuming the value of R, the gas constant. Likewise it can be used to find J when the two specific heats are known.

Adiabatic transformations. In the study of the specific heat of gases, it is necessary to consider also changes in volume and pressure of a gas under conditions of *thermal isolation i.e.,* when no heat is allowed to enter or leave the gas. Such changes are called *adiabatic transformations* (adiabatic = heat not passing through) in order to distinguish from the ordinary *isothermal transformations*, where the gas undergoes changes in pressure and volume under thermal communication with the surroundings so as to keep the temperature constant.

Considering unit mass of an ideal gas, let dQ be the amount of heat supplied to it, which will cause the gas to expand as well as increase in temperature. Let dT and dv be the resulting change in temperature and volume respectively.

Dealing with the two effects separately, let us suppose that first the temperature alone increases by dT, the volume remaining constant, and then the volume increases by dv at the increased temperature.

The amount of heat spent on increasing the temperature by dT of unit mass of the gas, kept at constant volume $= \text{C}_v.d\text{T}$ calories, where C_v is the specific heat at constant volume.

The amount of heat spent in the work done by the gas in expanding through dv against the external pressure p

$$= p\,dv \text{ ergs} = \frac{p\,dv}{J} \text{ calories.}$$

Since the heat dQ supplied is all spent in these two ways,

$$dQ = C_v.dT + \frac{p\,dv}{J}$$

If dQ and $C_v.dT$ are measured in mechanical units, or if $p\ dv$ is expressed in thermal units, we get

$$dQ = C_v.dT + p\,dv \qquad \dots (1)$$

This is a *fundamental equation*, which in combination with $pv = RT$ is capable of solving all problems concerning ideal gases.

Since in an adiabatic transformation, no heat can be supplied to the gas from outside, the above relation with $dQ = 0$ will represent such a transformation.

$$\therefore \qquad C_v.dT + p\,dv = 0 \qquad \dots (2)$$

In order to find a relation between p and v we must eliminate T from (2) using the gas equation $pv = RT$. Differentiating this, we get

$$p\,dv + v\,dp = R\,dT$$

Substituting for dT in (2)

$$C_v\left(\frac{p\,dv + v\,dp}{R}\right) + p\,dv = 0$$

Replacing R by $C_p - C_v$,

$$C_v\left(\frac{p\,dv + v\,dp}{C_p - C_v}\right) + p\,dv = 0$$

$$\text{Or } C_v.p\,dv + C_v.v\,dp + C_p.p\,dv - C_v.p\,dv = 0$$

$$i.e., \qquad C_v.v\,dp + C_p.p\,dv = 0$$

$$\text{Or} \qquad v\,dp + \frac{C_p}{C_v}\,.\,p\,dv = 0$$

The quantity C_p/C_v which is the *ratio of the two specific heats* is usually reperesented by the symbol γ.

$$v\,dp + \gamma\,p\,dv = 0$$

Dividing throughout by pv,

$$\frac{dp}{p} + \gamma \frac{dv}{v} = 0$$

Integrating,

$$\log p + \gamma \log v = \text{constant}$$

Or

$$pv^{\gamma} = \text{constant} \qquad \ldots (3)$$

This equation gives the *adiabatic relation between p and v* for a perfect gas.

To find the *adiabatic relation between v and* T, using the gas equation

$$pv = \text{RT},\ p = \frac{\text{RT}}{v}$$

Substituting this in (3),

$$\frac{\text{RT}}{v} \cdot v^{\gamma} = \text{constant}$$

$$\text{RT}\, v^{\gamma - 1} = \text{constant}$$

Since R is a constant,

$$\text{T}\, v^{\gamma-1} = \text{constant} \qquad \ldots (4)$$

Similarly, to find *the adiabatic relation between p and* T, using the gas equation, $v = \frac{\text{RT}}{p}$. Substituting this in (3),

$$p \cdot \left(\frac{\text{RT}}{p}\right)^{\gamma} = \text{constant}$$

$$\text{R}^{\gamma}\text{T}^{\gamma} \cdot p^{1-\gamma} = \text{constant}$$

$$\text{T}^{\gamma} \cdot p^{1-\gamma} = \text{constant}$$

$$\therefore \qquad \text{T}\, p^{\frac{1-\gamma}{\gamma}} = \text{constant} \qquad \ldots (5)$$

Relations (3), (4) and (5) are the three forms in which adiabatic transformations of a perfect gas can be represented. The chief interest in these relations at this stage lies in the fact that they offer a means of determining the specific heats of a gas. If the ratio of the two specific heats, $\gamma = \text{C}_p/\text{C}_v$, is experimentally determined, then C_p or C_v can be readily found, knowing one of them.

Ratio of the two specific heats in terms of the two elasticities of a gas. It is useful here to note the relation that exists between the ratio of the two specific heats and the ratio of the two elasticities of a gas, *viz.*,

$$\frac{\text{adiabatic elasticity}}{\text{isothermal elasticity}} = \gamma = \frac{C_p}{C_v}.$$

This relation can be established as follows :—

For *isothermal changes*, we have pv = constant

Differentiating, we get

$$v \, . \, dp + p \, dv = 0$$

Or $$v \, . \frac{dp}{dv} + p = 0$$

Or $$p = - v \, . \frac{dp}{dv} = \frac{dp}{-dv/v}$$

Now the *isothermal elasticity* E_i, involved here, is by definition,

$$E_i = \frac{\text{stress}}{\text{strain}} = \frac{dp}{-dv/v}$$

Hence $$E_i = p$$

For *adiabatic changes*, we have pv^γ = constant

Differentiating, we get

$$v^\gamma \, . \, dp + p\gamma \, v^{\gamma-1} \, . \, dv = 0$$

Dividing throughout by $v^{\gamma-1}$,

$$v \, . \, dp + \gamma p \, . \, dv = 0$$

Or $$\gamma p = - v \, . \frac{dp}{dv} = \frac{dp}{-dv/v}$$

Now the *adiabatic elasticity* E_a, involved here, is, by definition,

$$E_a = \frac{\text{stress}}{\text{strain}} = \frac{dp}{-dv/v}$$

Hence $$E_a = \gamma p$$

$$\therefore \frac{\text{Adiabatic elasticity } (E_a)}{\text{Isothermal elasticity } (E_i)} = \frac{\gamma p}{p} = \gamma = \frac{C_p}{C_v}.$$

The experimental methods of finding the specific heats of gases may be classified as under :—

(*i*) measurement of C_v

(*ii*) measurement of C_p

(*iii*) measurement of γ.

Determination of C_v, the specific heat at constant volume.

1. Joly's differential steam calorimeter. This apparatus, first devised by Prof. Joly as an improved form of the simpler model working on the same principle (already described *Cf.* p. 122), offers a *very accurate means of direct determination of C_v at ordinary temperatures.*

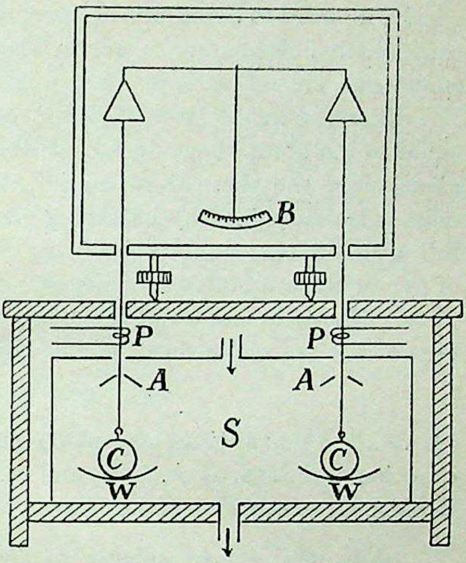


Fig. 61. Differential steam calorimeter.

Two equal hollow spheres of copper CC are suspended inside the same steam chamber S, from the two pans of a sensitive balance B by means of two fine wires. (Fig. 61). The spheres are provided with small pans of equal mass WW to catch the drops of water resulting from condensation of steam on the spheres. Two covers AA are arranged over the spheres to prevent any drops of water condensed on the walls of the steam chamber itself from falling on the spheres. The holes through which the suspension wires leave the steam chamber are lined with plaster of Paris to prevent the formation of drops of water at the holes which would interfere with the proper swinging of the balance and make accurate weighing difficult. A further precaution is taken by placing two electrically heated coils PP round the suspension wire just over the holes to quickly evaporate any water which the plaster lining cannot absorb.

Both the spheres are exhausted and the balance is counterpoised. Then one of them is carefully filled with the gas to be experimented upon, pure and dry, at any desired pressure and counterpoised against the empty sphere to obtain the mass m of the gas used. After allowing the gas to attain the temperature of the surroundings, its initial temperature θ_1 is noted with a standard sensitive mercury thermometer inserted in the chamber. Steam is then admitted into the chamber where it condenses on both the spheres until they rise to the temperature of steam. Steam is allowed to get into the chamber first with a good pressure and then more gently, in order to avoid unnecessary condensation of steam. Greater condensation occurs on the sphere which contains the gas than on the empty one, since heat is required to raise the temperature of the gas. The difference in the mass of steam condensed on the two spheres is equal to the mass of condensed steam required to heat up the gas alone, since the thermal capacities of the spheres are equal. This mass w is determined by balancing once again, while the chamber is full of steam, the counterpoise being checked a few times at intervals of two or three minutes to make sure that the condensation is complete. The temperature of the steam θ_2 is also noted. The specific heat of the gas at constant volume is readily found from the relation

$$m\mathrm{C}_v\,(\theta_2 - \theta_1) = w\mathrm{L}$$

where all the quantities except C_v are known either by the actual experimental data, as m, θ_1, θ_2 and w, or by assumption, as L, the latent heat of steam. Hence C_v can be estimated.

Joly used copper spheres of diameter 6·7 cms. and weighing 92·2 gms. Experimenting on air, at different pressures, one set of data was as follows : pressure of enclosed air = 20 atmospheres ; mass of air enclosed (m) = 4 gms. ; mass of steam condensed (w) = 0·12 gm. ; initial temperature (θ_1) = 15°C, final temperature (θ_2) = 100°C.

The *great advantage* of the differential calorimeter is that any source of error common to the two spheres, such as effect of buoyancy and thermal capacity of the container is practically eliminated. However, to obtain accurate results, several corrections have still to be applied for :—(*i*) the thermal expansion of the container and the consequent work done by the gas in expanding to this increased volume ; this correction can be estimated from the knowledge of the coefficient of expansion of copper and the initial and final pressures of the gas ; (*ii*) the increased pressure of the gas as the temperature rises with the resulting dilatation of the container ; (*iii*) the buoyancy arising from the increased volume of the sphere, both in air at θ_1°C and in steam at θ_2°C ; (*iv*) the unequal thermal capacities of the two spheres; this is done by repeating the experiment with the spheres interchanged ; (*v*) reducing the weight of the condensed steam to that in vacuum.

2. Pier's explosion bomb method. For the determination of C_v *at high temperatures* up to 3000°C, Pier has devised the modern

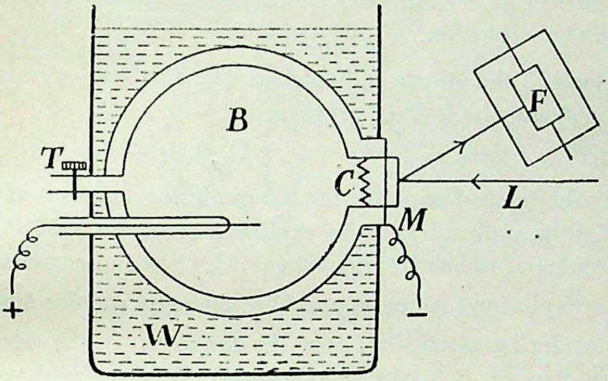


Fig. 62. Pier's explosion bomb.

explosion bomb method, illustrated in Fig. 62. A steel bomb B provided with a side tube T through which it can be evacuated and filled with various gases at any desired pressures is immersed in a water bath W. The wide mouth of the bomb is closed by a corrugated steel membrane C, to the front of which is attached a plane mirror M. A parallel beam of light L is made to fall on M where it is reflected and finally forms an image on a sensitive photographic film F, which revolves on a drum. The pressure attained in an experiment can be found from the record of the deflected light spot on the film. The gas to be experimented upon and an explosive mixture, say a mixture of oxygen and hydrogen, are introduced into the bomb. Their partial pressures are known. The experimental gas must be "inert" *i.e.*, it should not take part in a reaction either from want of chemical affinity or due to an excessive amount. The explosion is made by means of electric sparks produced between two electric terminals, one of which is arranged inside the bomb while the other is fixed to the side of the bomb. The released heat of reaction raises the temperature of the gas under investigation. The maximum temperature reached by the gas is estimated from the final pressure reached in the explosion, faithfully recorded on the film. Assuming the laws of perfect gas, it can be shown that

$$t_2 = \left(\frac{P}{e} - 1\right)(273 + t_1) + t_1$$

where t_1 is the initial temperature, as indicated by a thermometer immersed in the bath W, t_2 the final temperature, P the ratio of explosion pressure to initial pressure and e the ratio of final number of molecules to initial number, since the total number of molecules changes in the explosion.

Neglecting the effects of heat loss, the relation connecting the specific heats and the heat of reaction is

$$m\,Q = (m\,C_{v_e} + n\,C_{v_g})\,(t_2 - t_1)$$

where Q is the heat of reaction for the explosion mixture at t_2, m the number of gram molecules of the explosion products, n the number of gram molecules of the experimental gas, C_{v_e} the mean molar specific heat of the explosion products, and C_{v_g} the mean molar specific heat of the gas under investigation, over the range $(t_2 - t_1)$. Hence if Q and C_{v_e} are known, C_{v_g} can be calculated. Q is easily obtained from thermochemical data. C_{v_e} can be determined by exploding different amounts of a gas whose variation of specific heat with temperature is known.

Corrections have to be made for loss of heat, effects of dissociation and incomplete combustion. The chief disadvantage of the method is that it directly gives only the average value of specific heat over a wide range of temperature and not the value at any particular temperature.

3. **Nernst vacuum calorimeter** is used for measuring C_v *at low temperatures*, as indicated on p. 118. The gas is enclosed in the second type of calorimeter meant for bad conductors and the experiment carried out as already described. Eucken employed this method to investigate the specific heat of hydrogen in the range 35° and 273°K.

Determination of C_p, the specific heat at constant pressure. 1. The method of mixtures. *Regnault* devised an elaborate apparatus to determine the C_p of gases by the method of mixtures. (Fig. 63).

The gas under investigation is stored, pure and dry, in a reservoir R which is kept immersed in a constant temperature water-bath. The pressure of the gas in the reservoir is measured by a mercury manometer M_1 attached to the delivery tube. By opening the tap T and adjusting the screw valve V to give a suitable difference in levels in the manometer M_2, the gas is allowed to flow through the apparatus at a constant rate. The pressure of the flowing gas is kept constant throughout the experiment by maintaining the difference in

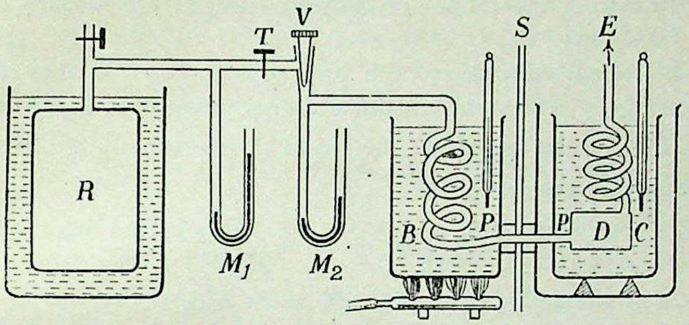


Fig. 63. Regnault's apparatus for C_p.

levels of M_2 the same throughout, which can be done by opening V more and more as the pressure of the gas in R goes down. The gas, thus maintained at constant pressure, flows through the spiral tube immersed in a heated oil-bath B whose temperature is kept constant at any desired value as indicated by a thermometer placed in it. The spiral is long enough for the gas passing through it to attain the temperature of the bath. The gas then enters a condenser D placed in a calorimeter C, heats up the water in the calorimeter and finally goes out through the exit tube E, after having been cooled down to the temperature of the calorimeter and contents. In order that the heated gas may not lose any heat when it passes from the hot oil-bath into the calorimeter, the passing tube PP is made of non-conducting material ; likewise to protect the calorimeter from receiving heat from the oil-bath the calorimeter is supported inside a wooden case and a wooden screen S is interposed between the bath and the calorimeter.

If m be the mass of gas that flows into the calorimeter, θ_1 the temperature of the oil-bath, M the mass of water used in the calorimeter, w the water equivalent of the calorimeter, condenser, etc., θ_2 and θ_3 the initial and final temperatures of the calorimeter and contents and C_p the specific heat at constant pressure of the gas, the heat lost by the gas $= mC_p\left(\theta_1 - \frac{\theta_2 + \theta_3}{2}\right)$, since the gas, flowing at a constant rate, cools on the average from θ_1 to $(\theta_2 + \theta_3)/2$; the heat gained by the calorimeter and contents $= (M + w)(\theta_3 - \theta_2)$.

$$\therefore mC_p\left(\theta_1 - \frac{\theta_2 + \theta_3}{2}\right) = (M + w)(\theta_3 - \theta_2),$$

from which C_p can be calculated.

The *mass m of the gas which has been used* is found, by noting the initial and final pressures of the reservoir with the manometer M_1 and knowing the volume of the reservoir and the density of the gas.

Let v and θ be the volume and temperature of the reservoir respectively, p_1 and p_2 the initial and final pressure of the reservoir.

If ρ_1 be the density of the gas in the reservoir at the beginning, then applying the gas laws,

$$\frac{p_1}{\rho_1} = R\,(273 + \theta) \text{ or } \rho_1 = \frac{p_1}{R\,(273 + \theta)}$$

Similarily, if ρ_2 be the density at the end,

$$\frac{p_2}{\rho_2} = R\,(273 + \theta) \text{ or } \rho_2 = \frac{p_2}{R\,(273 + \theta)}$$

$$\therefore \qquad \rho_1 - \rho_2 = \frac{p_1 - p_2}{R(273 + \theta)}$$

The mass m of the gas that has escaped from the reservoir during the experiment is given by $m = (\rho_1 - \rho_2)v$.

$$\therefore \qquad m = v \times \frac{p_1 - p_2}{R(273 + \theta)}$$

If ρ is the density of the gas at N.T.P.,

$$\frac{76}{\rho} = R \times 273 \text{ or } R = \frac{76}{\rho \times 273}$$

Substituting this value of R

$$m = v \cdot \frac{273}{273 + \theta} \cdot \frac{p_1 - p_2}{76} \cdot \rho$$

Hence, knowing p_1 and p_2 (which are in cm. of mercury), v, θ and ρ, m can be calculated.

The initial and final temperatures of the calorimeter θ_2 and θ_3 are noted with a sensitive thermometer. *The final temperature θ_3 must be corrected for "radiation"* as follows :—

In the experiment the calorimeter and contents not only lose heat in the usual way, but also receive heat by conduction along the tube leading out of the oil-bath and by convection, etc. from the screen S. The second factor is the greater and hence θ_3 is higher than the correct value. The quantity $\delta\theta$ to be subtracted from it to obtain the true value is estimated in the following way :—

The rise in temperature of the calorimeter is measured for 10 minutes before the flow of gas is started. The actual flow of gas is then allowed for 10 minutes, when it is shut off and the rise in temperature of the calorimeter is measured for another 10 minutes. During the first and last periods, the calorimeter has been receiving or losing heat from the various sources stated above and the average of the two rises in temperature is equal to the required radiation correction $\delta\theta$. Introducing this correction,

$$mC_p\left(\theta_1 - \frac{\theta_2 + \theta_3}{2}\right) = (M + w)\{(\theta_3 - \delta\theta) - \theta_2\}$$

It is assumed that the gas enters and leaves the calorimeter at constant pressure. Actually, a slight difference of pressure, about 1 mm. of mercury, is observed. The error thus introduced is however less than the other experimental errors and hence can be neglected.

It may be noted that Regnault's method is well suited for determining *C_p at ordinary pressures.* Lussana devised *a high pressure apparatus*, in which, though the basic principle is the same as that of Regnault, but unlike Regnault's technique, the same amount of gas enclosed at a high pressure is repeatedly heated and passed through the calorimeter. The chief advantages of this improved technique are :—(*i*) the gas is not wasted, since the same mass of gas can be used over and over again, (*ii*) the pressure of the gas can be maintained constant throughout, and (*iii*) the specific heat of gases at very high pressures can be found.

For determining *C_p at high temperatures* Holborn and Henning designed an apparatus which, though based on the method of mixtures, employs electric heater, thermocouple thermometer and special calorimeter. The gas is heated by passing it through a spiral placed in an electric oven and then through a transit tube which is also electrically heated. The temperature of the gas just as it enters the calorimeter is measured by a thermocouple. The condenser in the calorimeter is made of silver and packed with silver filings. Gas is passed through the calorimeter till the silver filings attain the temperature of the gas. An electric stirrer is used to enable quick and uniform distribution of temperature in the calorimeter. With such a device, the C_p of nitrogen, carbon dioxide and steam up to 1400° C have been determined. Nernst has used the same arrangement for finding the specific heat of ammonia upto 600°C. It must be said that in this method the calorimeter corrections are uncertain and difficult.

2. The electrical continuous flow method. The continuous flow calorimetry, first devised by Callendar and Barnes for finding the mechanical equivalent of heat and for studying the variation of the specific heat of water with temperature, as already indicated, was applied by Callendar and Swann to the determination of C_p of a gas. Subsequently Scheel and Heuse refined the technique in such a way as to employ it in *finding C_p of a gas down to very low temperatures.* We shall here give an outline of this most recent form of apparatus.

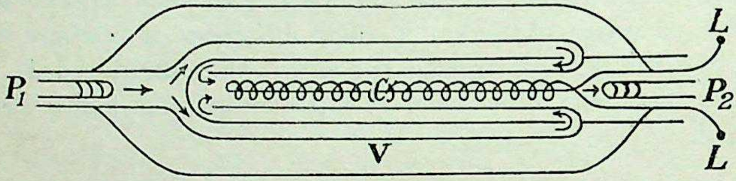


Fig. 64. Scheel and Heuse continuous flow method for C_p.

The gas after passing by a platinum resistance thermometer P_1 is made to circulate at a constant rate through a long glass tube in the direction indicated by the arrows. Then it passes over the heater coil C, electrically heated by means of the leads LL, where its temperature is raised. Finally it flows past a second platinum resistance thermometer P_2 and leaves the apparatus. The tube through which the gas circulates is surrounded by a vacuum jacket V, which makes the cooling correction negligible; if any heat should still escape from the gas in contact with the heater coil, it is taken up by the succeeding stream of gas which is coming in through the inner passage to the heater coil, so that all the heat is retained by the gas without escaping. The whole apparatus is surrounded by a water-bath, not shown in figure.

When the steady state is reached, the constant rise in temperature of the gas is found by taking the readings of the two platinum resistance thermometers P_1 and P_2 at the entry and exit respectively.

The specific heat of the gas C_p is given by the relation

$$\frac{\mathrm{EI}t}{\mathrm{J}} = m \,.\, C_p\,(\theta_2 - \theta_1)$$

where E is the P.D. between the ends of the heater coil, I the current flowing in the coil, t the time for which the current is passed, J the mechanical equivalent of heat, m the mass of gas passing through the apparatus for time t, θ_1 the temperature of the gas at entry and θ_2 at exit. It has already been indicated how the various quantities E, I, t are measured (*Cf.* p. 135). The mass m of the gas used is estimated by discharging the outflowing gas into a eudiometer and measuring the volume collected.

The chief advantages of the method have also been given (*Cf.* p. 136).

For *work at low tempertaure*, the gas is initially passed through a low temperature bath in which the whole apparatus is also immersed. In the case of helium and other rare gases, Scheel and Heuse further modified the apparatus so as to have a closed circuit. These workers experimented on various gases in the range 0°C to — 180°C.

It may be noted that Holborn and Jakob have employed this method for finding the specific heat of gases at high pressures with excellent results.

Determination of γ, the ratio of specific heats. Although the ratio γ of the two specific heats of gases offers an indirect means of finding the specific heats, some of the methods of determining γ are so accurate that the actually accepted values of C_p and C_v are based on the values of γ.

The methods of measurement of γ may be grouped under two heads, *viz.* (*i*) those based on the *adiabatic expansion or compression* of a gas ; (*ii*) those based on the *velocity of sound* in a gas. To the former category belong the methods of Clement and Desormes and of Partington, while to the latter, methods of direct determination of velocity of sound in air and Kundt's tube method for other gases.

1. Clement and Desormes' method. Clement and Desormes were the first to determine γ by the adiabatic expansion method.

Principle. When a given mass of gas is subjected to an *adiabatic* change, its initial pressure p_0 becomes p_1 its initial volume v_0 becomes v_1, governed by the relation

$$p_0 v_0^{\gamma} = p_1 v_1^{\gamma}$$

$$\therefore \quad \frac{p_1}{p_0} = \left(\frac{v_0}{v_1}\right)^{\gamma} \text{ or } \frac{\log_e p_1}{\log_e p_0} = \gamma \cdot \log_e \frac{v_0}{v_1}$$

$$\therefore \quad \gamma = \frac{\log_e \dfrac{p_1}{p_0}}{\log_e \dfrac{v_0}{v_1}} \qquad \dots (1)$$

In the adiabatic change, the initial temperature T_0 also changes to T_1. If the gas is now allowed to return slowly from T_1 to T_0, without any change in volume which remains v_1, then its pressure will change from p_1 to p_2, given by the relation

$$p_0 v_0 = p_2 v_1$$

$$\therefore \qquad \frac{v_0}{v_1} = \frac{p_2}{p_0}$$

Substituting this value of $\frac{v_0}{v_1}$ in (1), we get

$$\gamma = \frac{\log_e \dfrac{p_1}{p_0}}{\log_e \dfrac{p_2}{p_0}} = \frac{\log_e p_1 - \log_e p_0}{\log_e p_2 - \log_e p_0} \qquad \ldots (2)$$

Hence, if we know the initial pressure p_0, the pressure p_1 after an adiabatic change and the final pressure p_2 of the gas, γ can be found.

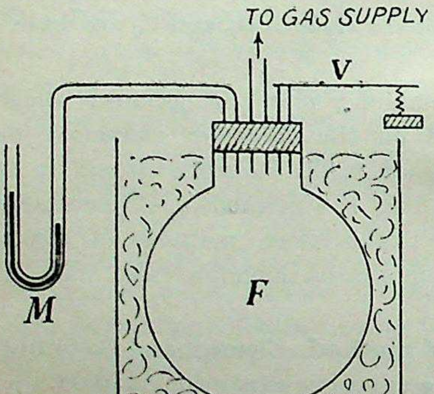


Fig. 65. Apparatus of Clement and Desormes.

Experiment. A large flask F of about 20 to 30 litres capacity, with its mouth closed air-tight, but fitted with suitable tubes for admitting the gas under investigation, for connecting an oil or sulphuric acid manometer M and for arranging a valve V which can be suddenly opened and closed by a spring lever, is placed inside a wooden box packed with cotton wool, as shown in Fig. 65. The large capacity of the flask is to reduce the loss of heat by convection and conduction with the surroundings; the same purpose is served by the cotton-wool packing, so that conditions required for an adiabatic change are realised as nearly as possible. The tube to which the valve is fixed must be wide enough to allow the gas to expand sufficiently suddenly for the expansion to be adiabatic. A water manometer is not to be used, since the flask has to contain only the gas, pure and dry, and not a mixture of the gas and water vapour.

The flask is filled with the gas at a pressure slightly greater than that of the atmosphere. The steady difference in levels h_1 of the manometer is noted. A jerk is given to the valve V, so that the gas inside expands *adiabatically* to atmospheric pressure, by being put in communication with the outside for a very brief interval. This adiabatic expansion causes the temperature of the gas to fall. The gas is left for some time to warm up to the temperature of the surroundings and the final steady difference in levels h_2 of the manometer is recorded.

If H represents the height corresponding to atmospheric pressure, intially, at temperature T_0, the pressure $p_0 = H + h_1$; after the adiabatic change, at temperature T_1, the pressure $p_1 = H$; after the final regaining of the temperature T_0, the pressure $p_2 = H + h_2$. Using relation (2)

$$\gamma = \frac{\log_e H - \log_e (H + h_1)}{\log_e (H + h_2) - \log_e (H + h_1)}$$

$$= \frac{\log_e (H + h_1) - \log_e H}{\log_e (H + h_1) - \log_e H - \{\log_e (H + h_2) - \log_e H\}}$$

$$= \frac{\log_e \dfrac{H + h_1}{H}}{\log_e \dfrac{H + h_1}{H} - \log_e \dfrac{H + h_2}{H}}$$

$$= \frac{\log_e \left(1 + \dfrac{h_1}{H} \right)}{\log_e \left(1 + \dfrac{h_1}{H} \right) - \log_e \left(1 + \dfrac{h_2}{H} \right)}$$

Since h_1 and h_2 are small compared with H,

$$\gamma = \frac{\dfrac{h_1}{H}}{\dfrac{h_1}{H} - \dfrac{h_2}{H}} = \frac{h_1}{h_1 - h_2}$$

Hence from the noted values of h_1 and h_2, γ is readily calculated.

This method is subject to the following serious error. We have assumed that, when the valve is jerked in order to put the gas inside in communication with the outside for a moment, the gas expands adiabatically to atmospheric pressure. Actually, however, this is not certain ; for, as soon as the valve is opened oscillations set in, as indicated by the manometer, which take some time to die out. Now since the valve is closed quickly, it is not possible to know the exact pressure at the end of the adiabatic expansion ; it may be greater or less than the atmospheric pressure. The ideal thing is to close the valve at the instant when during an oscillation the pressure is just equal to that of the atmosphere. But this is not easy to realise in practice.

This difficulty has been overcome by Lummer and Pringsheim and by Partington by measuring *the change in temperature due to the adiabatic expansion*, in which case, it is not necessary to close the valve. But it is essential that the temperature is measured immediately the expansion is completed and that the time taken for this measurement should be as short as possible. Clement and Desormes, thinking that such a thing was well nigh impossible in practice, had recourse to the ingenious alternative method of following the adiabatic change by an increase in pressure at constant volume until the gas rose again to its original temperature. Due, however, to the inherent defect stated above, the method is now only of historical and laboratory interest.

2. Partington's method. Joule was the first to study the change in temperature following an adiabatic expansion or compression. Lummer and Pringsheim designed an apparatus to measure γ by this means. Partington perfected the technique still further. We shall here describe only Partington's method.

Principle. If a given mass of gas, subjected to an adiabatic change, has its pressure altered from p_0 to p_1 and its temperature from T_0 to T_1 we can write

$$T_0^{\gamma}\, p_0^{1-\gamma} = T_1^{\gamma}\, p_1^{1-\gamma}$$

Taking logarithms,

$$(1-\gamma)(\log_e p_0 - \log_e p_1) = \gamma\,(\log_e T_1 - \log_e T_0)$$

$$\therefore \qquad \gamma = \frac{\log_e p_0 - \log_e p_1}{(\log_e p_0 - \log_e p_1) - (\log_e T_0 - \log_e T_1)}$$

Experiment. A large flask A of about 130 litres capacity, provided with (1) an expansion valve V of variable aperture manipulated by a spring lever, (2) an inlet tube I for filling with pure dry air which has passed through tubes of drying agents D and (3) a bolometer B with the sensitive platinum strip arranged at the centre, is used (Fig. 66). An oil manometer M measures the initial excess of pressure of the air in the flask over that of the atmosphere. The flask is kept immersed in a water-bath whose temperature can be measured

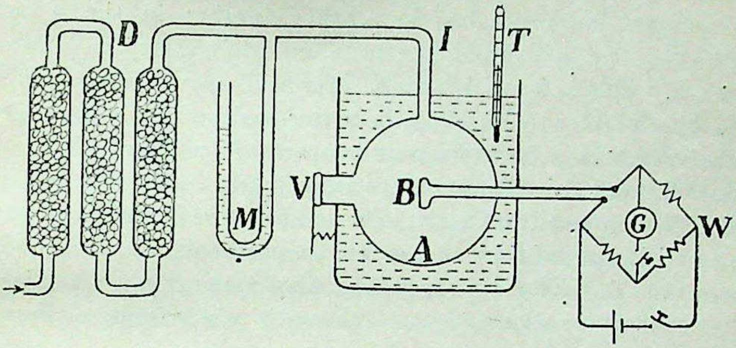


Fig. 66. Partington's apparatus.

by a carefully standardised thermometer T correct to 0·01°C. The bolometer is connected to one arm of a Wheatstone bridge W.

The flask must have a large capacity in order to reduce the thermal effects of conduction and convection in the gas. The bolometer must have a very small thermal capacity, and be free from "lag" and so constructed that the conduction of heat along the leads is eliminated. Partington secured these conditions by using a bolometer of very thin platinum wire, ·001 to ·002 mm. thick, with compensating leads. The galvanometer G used in the Wheatstone bridge must be capable of recording very rapid and small changes of current. An Einthoven string galvanometer, which has a very small period and reaches its steady deflection in 1/100th of a second, is used. With the help of the bolometer and the sensitive galvanometer the aperture of the expansion valve can be adjusted, so that no oscillations occur when the flask is put in communication with the outside, the pressure dropping rapidly to that of the atmosphere. If the aperture is too large, oscillations occur as indicated by the unsteady deflection of the galvanometer ; if it is too narrow, the decrease in pressure is too slow to be adiabatic. In practice, the aperture is gradually diminished until the galvanometer deflection is instantaneous and steady.

The initial pressure p_0 of the enclosed air is obtained by noting the difference in levels of the manometer M and the initial temperature T_0 is read from the thermometer T, when the flask has the same temperature as the water-bath. The valve V is opened and left open; the adiabatic expansion of the air causes a fall in temperature which is accurately measured by the following device. The balance of the bridge is upset in order to have a certain deflection in the galvanometer, which will be reduced to zero immediately after the adiabatic expansion. This is found by trials. Immediately after opening the valve, bits of ice are added to the water-bath, which is well stirred the whole time, in order to keep its temperature constant and equal to that following the adiabatic expansion, while keeping the galvanometer deflection steady at zero. The temperature of the bath under these conditions, read from the same thermometer, gives the final temperature T_1. The corresponding final pressure p_1, which is evidently the same as that of atmosphere, is read from a Fortin's barometer.

Thus knowing p_0 and p_1 and T_0 and T_1 (in absolute scale) γ is calculated from the relation derived above and is found to be 1·4034 at 17°C.

This method appears to be quite accurate since (*i*) the expansion is made as nearly adiabatic as can be realised in practice—it is only the expansion of the air in the neighbourhood of the bolometer that is needed to be adiabatic, while the rest of the large volume of air serves as a good heat insulation ; (*ii*) the temperatures before and after the adiabatic expansion can be accurately determined. It cannot be used, however, at high temperatures, since it is not possible to determine accurately the cooling correction.

3. Determination of γ from the velocity of sound. This method is based on the adiabatic expansion and compression of a gas involved in the propagation of sound, but differs from the previous methods in that no changes in pressure or temperature need directly be observed. The method is capable of giving *the most accurate results concerning the specific heats of gases for both high and low temperatures*. The fundamental assumption is that sound is *propagated adiabatically i.e.*, without any conduction of heat from the compressed to the rarefied portions of the gas medium, which is almost exactly verified for notes of high frequency.

Principle. The velocity of sound in any gas is given by the relation :

$$V = \sqrt{E_a/\rho}$$

where V is the velocity of sound, E_a the adiabatic elasticity and ρ the density of the gas.

But $$E_a = \gamma p \quad (c.f.p.\ 144)$$

$$\therefore \quad V = \sqrt{\gamma p/\rho}$$

Hence if the velocity of sound is measured in a gas of known density and pressure, γ of the gas can be calculated.

The velocity of sound in a gas can be determined either absolutely or relatively to that in a standard medium, such as air, which can be measured by other methods. The most accurate determination of the velocity of sound in air was made by Hebb in 1905 by a method based on the reflection of sound of known frequency between two parabolic mirrors 15 inches in diameter, placed 5 feet apart. The value obtained by him is 331·41 metres/sec. at 0°C and 76 cm. pressure.

It is to be borne in mind that, since most of the determinations of the velocity of sound in gases have been made *in tubes*, in the evaluation of γ by the relation given above where V refers to velocity of sound *in free space*, the velocity in the tube must be first reduced to the velocity in free space. This is done using the relation

$$V' = V(1 - kc) \qquad \dots (5)$$

where V' is the experimentally determined velocity in the tube, V the velocity in open space, k a constant depending on the radius, thickness, thermal conductivity, surface conditions of the tube as well as on the frequency of the sound, and c a factor depending on the viscosity, density, ratio of specific heats, etc., of the gas.

In practice, k is estimated with data for air, *i.e.*, by assuming the value of V from Hebb's experiment, observing V' for air and calculating c from the relation

$$c = \sqrt{\frac{\eta}{\rho}\left[1 + \sqrt{E}\left(\frac{\gamma - 1}{\sqrt{\gamma}}\right)\right]}$$

where η is the coefficient of viscosity of air, ρ the density of air, $E = K/\eta C_v$ (K the thermal conductivity, C_v the specific heat at constant volume) and γ the ratio of the specific heats of air.

The value of k thus obtained is used to find V, the velocity in free space, for any other gas.

Experiment. Several investigators have measured the velocity of sound in different gases over a wide range of temperature. Of these researches the most instructive are those of Kundt, and Partington and Shilling, which we shall briefly describe here.

(*a*) **Kundt's method.** Kundt first devised a simple apparatus ordinarily known as *Kundt's tube*, for finding the velocity of sound

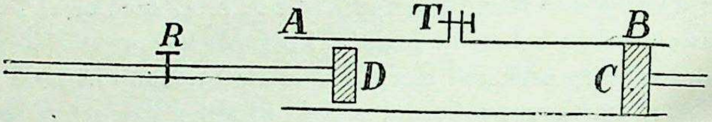


Fig. 67. Kundt's tube.

in a gas. It consists of a long and wide glass tube AB (about 1 metre in length, 3 cms. in diameter), provided with a narrow side tube T for the purpose of filling it with any gas. One end of the tube is closed tightly with a piece of cork C. Through the other end a loosely fitting disc D carried by a long glass or metal sounding rod R is introduced. The rod is clamped at its centre and it is seen that the disc D does not touch the sides of the tube (Fig. 67). Fine lycopodium powder is sprinkled within the tube as a streak along the length.

The free end of the sounding rod is stroked longitudinally, when a note of very high pitch is emitted by the longitudinal vibrations of the rod. When the rod thus vibrates, it sets up progressive waves in the gas column in AB which advance towards the closed end C, are reflected backwards and thus form stationary waves in the gas. If the gas column is excited to resonate with the sounding rod by adjusting the distance between C and D, the sound emitted will be very shrill and the lycopodium powder forms uniform striations perpendicular to the length of the powder streak. The distance between successive striations equals half the wave length of the sound wave in the gas. Hence knowing the frequency of the sound, the velocity in the gas is easily obtained. Circulating different gases through the tube, the velocity of sound in them can be determined in a similar manner.

Kundt later modified his apparatus into a *double tube arrangement*, by means of which the velocity of sound in any gas can be readily obtained, without even knowing the frequency of the source of sound, by simply comparing it with the known velocity of sound in air. This improved technique, shown in Fig. 68, consists of two tubes A and B connected by means of a single sounding rod R which is clamped at two points, one quarter of its length from the ends. Two rubber corks CC tightly fitting into the tubes serve also the purpose of the clamping arrangement.

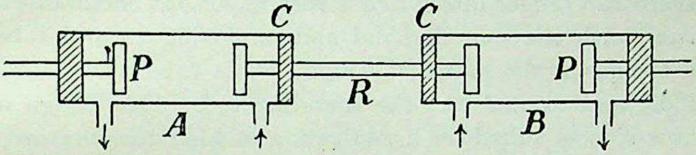


Fig. 68. Kundt's double tube apparatus.

The pistons PP introduced at the free outer ends of the tubes can be moved to and fro, in order to put the tubes in resonance with the sounding rod. Fine lycopodium powder is strewn all along the length of each of the tubes. Air is circulated through one of the tubes, and the gas under study through the other. The sounding rod is excited longitudinally by stroking it at the central portion and the pistons PP adjusted until well defined striations are formed in both the tubes. Measuring the distance between successive striations in each of the tubes, the wave lengths of the sound in air and in the experimental gas are found. Since the frequency of the sound which is equal to that of the sounding rod is the same for both the tubes, we have

$$\frac{V_{gas}}{V_{air}} = \frac{\lambda_{gas}}{\lambda_{air}}$$

Hence, knowing λ_{gas} and λ_{air} and assuming the value of V_{air}, V_{gas} can be calculated.

In order to get fairly accurate results, several *precautions* must be taken :—(*i*) The tubes and the lycopodium powder should be perfectly dry. (*ii*) Carefully purified air should be used. (*iii*) The tubes should be pretty wide, since decrease in diameter diminishes the velocity. (*iv*) Too much powder should not be used, as excess of it retards the velocity. (*v*) The velocity in the tube obtained from the experiment should be reduced to the velocity in free space.

Ramsay employed this method to determine the ratio of the specific heats of inert gases, such as argon, helium, etc. He obtained rather a low value, on account of certain difficulties, but still the results were sufficiently accurate to indicate that these gases were monatomic, an important clue in finding their atomic weight. Kundt and Warburg used the method for determining the ratio of the specific heats of mercury vapour and obtained the value 1·666.

Behn and Geiger introduced a very important modification, by dispensing with the sounding rod and employing a sealed tube containing the gas as the source of sound. This tube was clamped in the middle and excited like the sounding rod. This design of the apparatus is most suited for investigation at high temperature, provided the tube is properly chosen and its length is adjustable so that the enclosed gas may resonate easily with the sound given out by the tube. Later research workers, chiefly Partington and Shilling, used this improved form to determine the velocity of sound in different gases up to 1000°C.

(*b*) **Partington and Shilling method**. A silica tube AB, 230 cms. long and 4 cms. in diameter is wound over with a heater coil along its entire length (Fig. 69). One end of it is attached to a glass tube BC, 150 cm. long and about the same diameter, with an asbestos plug to prevent radiation of heat from the silica to the glass tube. Inside AB is a piston P of silica carried by a silica rod R, which is joined to a steel tube T by means of a cork. The other end of T carries an index I moving over a millimetre scale S, which enables to find the displacement of the piston. Through the tube T the leads of a thermocouple, used to measure the temperature of the gas in AB, are taken out to a potentiometer arrangement, (not shown in fig.). The end A of the silica tube is closed with a telephone diaphragm D which can be moved by means of a screw. A bell jar J is used to make this end gas-tight. The diaphragm is excited by a valve oscillator (not

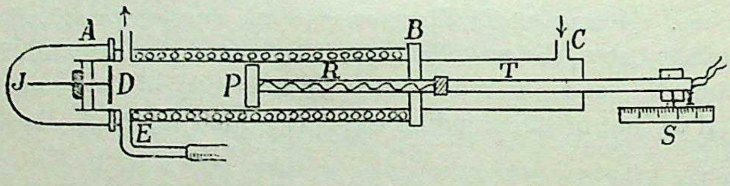


Fig. 69. Apparatus of Partington and Shilling.

shown in fig.) to give a note of high frequency, 3,000. The gas under investigation is made to circulate the apparatus through an inlet and outlet, indicated by arrows. At a side tube E, a rubber tubing is attached which leads to the ear of the experimenter.

Maintaining the gas enclosed in the silica tube at any desired temperature, the piston is moved away from the diaphragm by pulling out the silica rod attached to the steel tube and the readings of the index I on the scale corresponding to maximum sound heard through E are noted. The difference in the readings of I corresponding to successive maximum sounds gives half the wave length of the sound in the gas at the particular temperature chosen. Since the frequency is known, the velocity can be calculated. The position of D has to be adjusted at different temperatures in order to obtain maximum sound in E when it is at a distance of $\lambda/2$ from the latter.

Cook, replacing the heater coil by a long Dewar flask containing liquid air, was able to find γ for air and oxygen at *low temperatures* up to 90°K.

Results. (*i*) Some of the **important results** obtained are given in the following table, *as molecular heat in calories at 20°C and atmospheric pressure.*

Gases		C_v	C_p	$\gamma = C_p/C_v$
Monatomic	Argon	2·98	4·97	1·666
	Helium	2·98	4·97	1·666
Diatomic	Hydrogen	4·88	6·87	1·408
	Oxygen	5·04	7·03	1·396
	Nitrogen	4·96	6·95	1·402
	Nitric oxide	5·10	7·10	1·390
	Carbon monoxide	4·98	6·97	1·400
	Chlorine	6·15	8·29	1·350
	Air	4·96	6·95	1·402
Triatomic	CO_2	6·80	8·83	1·300
	SO_2	7·50	9·65	1·290
	H_2S	6·20	8·30	1·340
Polyatomic	Ammonia	6·55	8·80	1·320
	Methane	6·50	8·50	1·310
	Ethane	10·30	12·36	1·200
	Acetylene	8·40	10·45	1·240
	Ethylene	8·20	10·25	1·130

(*a*) It is seen that *the specific heat at constant pressure* (C_p) *is substantially greater than that at constant volume* in all cases, as is to be expected. It will be noted also that the *values of both C_v and C_p increase with the complex constitution of the gases*. Thus for monatomic gases, $C_v = 2{\cdot}97$, $C_p = 4{\cdot}97$; for diatomic gases, $C_v \approx 5$, $C_p \approx 7$; for triatomic gases, $C_v \approx 6{\cdot}5$, $C_p \approx 8{\cdot}5$; for polyatomic gases, $C_v \geqslant 6{\cdot}5$, $C_p \geqslant 8{\cdot}5$. The kinetic theory of gases, while justifying these experimental results, predicts that C_v and C_p should be independent of temperature, contrary to experimental findings. This point has to be considered somewhat in detail.

(*b*) *Variation of the specific heats of gases with temperature.* For a number of gases C_v *is found to be independent of temperature in the ordinary range* of temperature, while in the case of *monatomic gases throughout the whole range of temperature*, in consonance with the conclusions of the kinetic theory. But at *high temperatures*, the molecular heats of *gases that are not monatomic show a very significant increase*. Thus, for hydrogen, at 0°C, $C_v = 4{\cdot}75$ and at 2000°C, $C_v = 6{\cdot}5$; for oxygen C_v is 5·17 at 300°C, 5·35 at 500°C and 6 at 2000°C. At *low temperatures*, the discrepancy is still more marked. Measurements made by Nernst, Eucken and others have shown that for hydrogen and oxygen, C_v decreases steadily tending towards the limiting value of 2·98 calories, valid for monatomic gases, at about 40°K. There are reasons to believe that at sufficiently low temperatures all gases have the same value for C_v, as that of the monatomic gas. Further the value of C_v increases with rise of temperature and decreases with fall of temperature in a manner which cannot be explained by the classical theory. As in the case of solids, the *quantum theory* has been applied by Einstein here also, with a certain amount of success.

For gases, the molecules are sufficiently far apart and the different types of motions *viz.*, translational, rotational and vibrational, can be assumed to be independent of each other. The total energy of a gram-molecule, which will be the sum of the energies of the individual molecules, can be put as the sum of the energies due to translation, rotation and vibration. In consequence three terms will go to make up the molecular heat C_v, which can be expressed as

$$C_v = C_t + C_r + C_o$$

which C_t, C_r and C_o represent the contributions from translational, rotational and vibrational motions respectively.

All gases must have energy due to translational motion, which according to the classical theory is about 2·98 calories. This is the lowest value of the molecular heat for any gas. The quantum laws cannot be applied to this energy, since the motion is not periodic. But the energies due to rotation and vibration, being periodic, can be quantised, *i.e.*, they occur in discrete quanta, in a discontinuous manner. At low temperatures, the total molecular energy is very much less than the minimum energy required for rotation or vibration according to quantum law ; hence rotation and vibration are absent at such temperatures, so that C_v has only the value of C_t which is equal to 2·98 calories, as experimentally found in the case of all monatomic gases and of polyatomic gases at very low temperatures. As the temperature increases, rotation develops progressively, molecule after molecule within the gram-molecule beginning to rotate, so that C_v rises gradually to the value $C_t + C_r$, where it remains steady until, due to further rise in temperature, atomic vibrations inside the molecules set in. Thereupon there is another increase in the value of C_v till it reaches the final steady value of $C_t + C_r + C_o$.

(*ii*) **Specific heat of vapours** is of interest as we shall see presently. It is necessary to consider this point under the following two categories :—

(*a*) *Specific heat of non-saturated vapour.* Regnault determined the specific heat of superheated or non-saturated steam and other vapours with his apparatus as follows. Steam is superheated to θ_1°C by passing it through the spiral in the oil-bath kept at a temperature higher than 100°C. The superheated steam is next passed under constant pressure into the condenser kept immersed in the water calorimeter. The initial temperature θ_2°C and the final temperature θ_3°C of the calorimeter and contents are noted.

Let the mass of steam condensed be m gms., the latent heat of steam at the condensing point θ°C be L calories, the mass of water in the calorimeter be M gms. and the water equivalent of the calorimeter and contents be w gms.

The total quantity of heat evolved is given by

$$m\,C_p\,(\theta_1 - \theta) + m\,L + m\,(\theta - \theta_3)$$

The total quantity of heat absorbed by the calorimeter and contents is $(M + w)\,(\theta_3 - \theta_2)$

$$\therefore\ m\,C_p\,(\theta_1 - \theta) + m\,L + m\,(\theta - \theta_3) = (M + w)\,(\theta_3 - \theta_2)$$

The experiment is repeated with another value for θ_1 and a second equation, similar to the above, is obtained. Solving the two equations C_p and L are determined for the temperatures chosen. The value of C_p thus obtained for steam, in the range 125°C — 225°C is 0·48.

In determining the specific heats of vapours of other liquids, the fact that the specific heat of any liquid other than water is not unity must be taken into account. Consequently the final relation to be used will assume the form

$$m\,C_p\,(\theta_1 - \theta) + m\,L + ms\,(\theta - \theta_3) = (M + w)\,(\theta_3 - \theta_2)$$

where s is the mean specific heat of the liquid used.

Further, the experiment has to be repeated thrice with three different values for θ, and the three equations thus obtained are solved for C_p, L and s.

(*b*) *Specific heat of saturated vapour.* When a saturated vapour is heated at constant pressure or at constant volume it becomes non-saturated. Hence the specific heat in the case of a saturated vapour can be neither C_p nor C_v. It has to be defined as the quantity of heat required to raise unit mass of the saturated vapour through 1°C, the pressure being suitably increased and the volume proportionately decreased, so that the whole mass of the vapour remains saturated.

Considering unit mass of a saturated vapour at θ°C, let its temperature be raised to $(\theta + 1)$°C, while at the same time its pressure increased in such a way that it remains saturated. Due to the increase of pressure involved in the process, a certain amount of external work has been done on the vapour which appears as heat. If the *thermal equivalent of the external work* done on the vapour is *sufficient* to raise the temperature of the vapour by 1°C, no further heat is required to raise the temperature and hence the *specific heat of such a saturated vapour must be equal to zero*. Such a case has not been found to exist. If the *thermal equivalent* of the work done on the vapour is *less* than the heat required to raise the temperature by 1°C, the balance has to be supplied to the vapour, in which case the *specific heat is positive*. Such vapours exist, *e.g.*, ether vapour. Finally, if the *thermal equivalent* of the work done on the vapour is *greater* than that required to raise the temperature by 1°C the excess has to be removed in order to keep the vapour saturated, in which case the *specific heat is negative*. Such is the case with *saturated steam*, *i.e.*, saturated steam gives out heat when its temperature is raised. We shall come back to these interesting phenomena later.

Practical Applications. We shall conclude this chapter on specific heat by citing a few interesting applications :

(*a*) *Calorimeter method of measuring high temperature.* A known mass of a suitable solid, such as platinum whose melting point is very high (1670°C) and whose specific heat varies least with temperature, is placed in the furnace, the unknown high temperature of which is to be determined. When it has acquired the temperature of the furnace it is transferred to a water calorimeter. Using the method of mixtures, from the data of the experiment, the temperature of the furnace can be found.

(*b*) *Calorific value of fuels—calorimetric bomb.* The value of fuels such as coal, petrol, etc., is judged mainly from the quantity of heat produced by the combustion of a given weight of them. It is known as the *calorific value* and is expressed either in *major calories per gram* or *in B. Th. U. per pound.* It is not easy to measure *accurately* this quantity and several types of calorimeters have been devised for the purpose. The *calorimetric bomb* is one such device. It consists of a thick steel cylinder S fitted with a tight lid L (Fig. 70). A screw valve G regulates the admission of oxygen through the tubes A and B into the cylinder ; pure oxygen is used instead of air, in order to secure rapid and complete combustion of the fuel. A similar screw valve H allows the gas products of combustion to go out of the cylinder. The fuel is placed in a platinum dish E and ignited by means of a platinum wire loop P, one of the leads of which passes through the centre of the lid, well insulated from the latter, to a terminal F, the other being connected to another terminal D. If the fuel is solid, like coal, it is ground to a fine powder and compressed into a briquette ; if it is liquid, like petrol, it is soaked in pure cellulose and used. To enable the bomb to withstand the corrosive action of the products of combustion it is gold plated inside. The bomb is enclosed in a water calorimeter provided with stirrer and an accurate mercury thermometer. The whole is surrounded by a constant temperature bath.

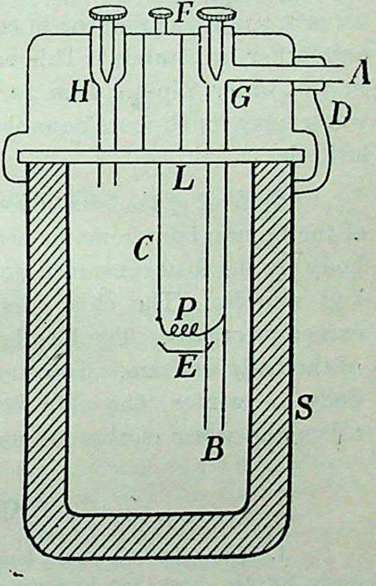


Fig. 70. Calorimetric bomb.

The oxygen, which is usually employed at a high pressure of about 20 to 25 atmospheres, not only causes instantaneous combustion, but also drives the products of combustion through the screw valve H, so that they bubble through the surrounding water, giving up their heat to it. The rise in temperature of the calorimeter is noted with the thermometer. Using the method of mixtures, from the experimental data, the calorific value of the fuel can be estimated. The results thus obtained for coal and petrol are 8·8 and 11·3 major-calories per gram respectively.

(c) *Effects of the high specific heat of water.* Owing to its high specific heat, water absorbs much more heat in warming and gives out much more heat in cooling than an equal mass of almost any other substance. This brings out the advantage of using water in hot-water pipes. Due to the same reason islands surrounded by water have much more equable climate than continents in the same latitude.

(d) *Heat of the human body.* In normal health, the temperature of the human body remains nearly constant. Heat is supplied to the body by the food consumed and by the oxidation of the living tissues and muscles. The chief loss of heat is through the skin and the excretory organs. The blood stream serves to keep the temperature of the body uniform. To counteract the greater loss of heat from the body in winter, the skin contracts of its own accord, more food is taken and warm clothes are used.

QUESTIONS

1. Enunciate Newton's law of cooling and show how corrections can be made for the heat lost by radiation in calorimetric experiments. Establish a relation for finding the specific heat of liquids by the method of cooling.
(Nagpur University)

2. Describe giving experimental details, how the specific heat of a solid is measured by the method of mixtures and explain how you apply radiation correction.
(Madras University)

3. Describe Bunsen's ice calorimeter and show how you would use it to find the specific heat of a metal in small bits.
(Madras University)

4. Describe the steam calorimeter and explain how it may be used to determine the specific heat of a small solid.
(Allahabad University)

5. Describe Nernst vacuum calorimeter and indicate briefly how it has been used for measuring specific heats at low temperatures.
(Allahabad University)

6. Describe Regnault's method of applying radiation correction in calorimetric experiments. *(Madras University)*

7. Give a critical discussion of the way in which our knowledge of the atomic heat of elements in the solid state has developed since Dulong and Petit's law was enunciated.

8. Indicate the manner in which the specific heat of a solid varies with temperature and outline the theory which explains this variation. *(Madras University)*

9. What difficulties present themselves in an attempt to measure the specific heat of metals at low temperatures ? Describe Nernst and Lindemann's work on this subject pointing out how they overcame the difficulties you have mentioned.

10. Discuss the various methods of measuring the specific heats of solids and liquids, pointing out the advantages and disadvantages of the various methods. *(Cambridge)*

11. Discuss the 'method of cooling' for the determination of specific heats and show that the method is not dependent on the truth of Newton's law of cooling. *(Cambridge)*

12. Describe the constant flow method of Callendar and Barnes for the measurement of the specific heat of a liquid.

A stream of water flows at a steady rate of 1 pint per minute through a copper pipe which is heated in the middle by a steady flame. The inlet and outlet temperatures are observed to be 10°C and 25°C respectively. Another liquid of specific gravity 0·8 is now passed through the tube at a steady rate of $\frac{1}{2}$ pint per minute and its initial and final temperatures are found to be 12°C and 61°C. Calculate the specific heat of the liquid. **Ans.** 0·77

13. Give a critical discussion of the evidence which has shown that the specific heat of water varies with temperature and state the conclusions which have been reached. How do the results affect the definition of the calorie ?

14. Describe Joly's differential steam calorimeter and explain how it is used for finding the specific heat of a gas at constant volume. State the corrections to be made. *(Madras University ; Calcutta University 1947, Patna University 1947 ; Gujerat University 1951 ; Punjab University 1952, 1954)*

15. Describe a method of determining the specific heat of a gas at constant volume, giving a neat diagram of the apparatus necessary. Why is the specific heat at constant pressure greater than that at constant volume ? *(Dacca University)*

16. Explain why the specific heat of a gas at constant pressure is greater than that at constant volume. Obtain an expression for the difference between the values for a perfect gas. Find the numerical value of their ratio for monatomic gases. *(Madras University ; Punjab University 1949, 1951 ; Utkal University 1952)*

17. Describe an accurate method of measuring the specific heat of a gas at constant pressure. *(Gujerat University 1949, 1951 ; Punjab University 1941)*

18. Give an account of the continuous flow method of measuring the specific heat of a gas at constant pressure and point out its advantages.

(*Allahabad University*)

19. Describe and discuss critically Regnault's and Callendar and Barnes' method of determining the specific heat of a gas at constant pressure.

(*Madras University*)

20. Show that for a perfect gas $C_p - C_v = R$. Calculate C_v for hydrogen given $C_p = 6{\cdot}85$ cal./gm. molecule, density of hydrogen at N.T.P. $= 0{\cdot}0899$ gm./litre and $J = 4{\cdot}18 \times 10^7$ ergs./cal. **Ans.** 4·87 cals./gm. mol.

(*Madras University*)

21. One litre of hydrogen at 0°C and 760 mm. pressure weighs ·0896 gm. The specific heat of hydrogen per gram at constant pressure and volume are 3·409 and 2·411 respectively. Calculate the value of J. Given $g = 981$ cms./sec.^{2} and density of mercury = 13 6 gm./1 c.c. **Ans.** $4{\cdot}15 \times 10^7$.

(*Punjab University 1955*)

22. Six litres of air at 0°C and atmospheric pressure is contained in a copper globe. The globe is immersed in dry steam at 100°C and 7·71 gms. of water condense on the globe. The mass of the copper globe is 400 gms. Calculate the specific heat of the air at constant volume. **Ans.** 0·171

(*Madras University*)

23. Calculate C_v for air given that $C_p = 0{\cdot}23$. Density of air at 27°C and standard atmospheric pressure = 1·18 gms./litre and $J = 4{\cdot}2 \times 10^7$ ergs/cal. **Ans.** 0·1618.

(*Punjab University 1941*)

24. Deduce from first principles the adiabatic equation of a perfect gas.

A motor car tyre is pumped to a pressure of 2 atmospheres at 15°C when it suddenly bursts. Calculate the resulting drop in temperature.

(*Allahabad University*)

25. Distinguish between adiabatic and isothermal changes and show that for an adiabatic change in a perfect gas pv^γ = constant where γ is the ratio of specific heats at constant pressure and constant volume respectively.

(*Allahabad University, 1952 ; Punjab University, 1954, 1960*)

26. Establish the equation connecting pressure, volume and temperature of a gas in adiabatic transformation.

A litre of air at 76 cm. of mercury and 30°C is adiabatically compressed to a pressure of 120 cm. of mercury. Calculate the new volume and rise of temperatures. **Ans.** 719·7 c.c. 142°C

(*Madras University ; Baroda University 1953*)

27. Describe the Clement and Desormes' method of finding the ratio of specific heats of air, giving the simple theory of the method. What are the objections to the method and what modifications and improvements have been proposed ? (*Madras University ; Punjab University 1953, 1958 ; Allahabad Uinversity 1950 ; Bihar Uinversity 1954 ; Utkal University 1955*)

28. Derive the relation between volume and temperature of a mass of a perfect gas undergoing adiabatic compression.

A quantity of dry air at 15°C is adiabatically compressed to $\frac{1}{4}$ of its volume. Calculate the final temperature given $\gamma = 1{\cdot}4$ and $4^{\cdot 4} = 1{\cdot}74$.

(*Delhi University ; Aligarh University 1948 ; Punjab University 1957*)

29. Determine γ of air from the following data :—Velocity of sound = 34215 cm. per sec. in air at 750 mm. at 17°C, density of air = ·00129 gm. per c.c. at N T.P., coefficient of expansion of air 1/273, $g = 981$ cm./sec², density of mercury = 13·6 gm. per c.c. **Ans.** 1·402. (*Manchester University*)

30. Derive the formula and describe Clement and Desormes' method for determining the ratio of specific heats of a gas. (*Delhi University*)

31. In one hour a petrol engine consumes 5 kilograms of petrol whose calorific value is 10.000 cals. per gm. Assuming that 25% of the total heat escapes with the exhaust gases, and that 12% of the heat is converted into mechanical energy, find the average horse power developed by the engine and the initial rate of rise of temperature of the engine per minute. Radiation losses may be ignored, and the water equivalent of the whole engine is 40 kilograms. **Ans.** 9·35 H.P., 13·1°C per min. (*Cambridge*)

32. Write notes on :—

(*a*) Variation of specific heat of water with temperature.

(*b*) Variation of specific heat of gases with temperature.

(*c*) Calorific value of fuels. (*Delhi University 1955*)

(*d*) Measurement of specific heat of liquid air.

CHAPTER IV

CHANGE OF STATE

FUSION, VAPORISATION, SUBLIMATION

Introduction. It is a matter of common experience that one and the same substance can exist in three different states, solid, liquid and gas, and the change from one state to another can be brought about by the application or withdrawal of heat. Thus, water can be in the form of *solid ice*, or *liquid water* or *gaseous steam*. When ice is heated it becomes water, which on further heating becomes steam. Conversely steam can be changed to water and water to ice by withdrawing heat. The change from the solid to the liquid state is known as **fusion** or **melting** or **liquefaction,** while the reverse change from the liquid to the solid state **solidification** or **freezing.** The change from liquid to vapour is known as **vaporisation** and the reverse process **condensation.** It is to be noted that we have used the terms "vapour" and "vaporisation" for the gaseous state into which the liquid changes and not the terms "gas" and "gasification". The distinction between a vapour and a gas will be dealt with later. For the present, it is enough to say that when a liquid is changed into the gaseous state, it becomes a "vapour", which possesses properties similar to those of a gas.

A considerable amount of heat is absorbed or liberated when a substance changes from one state to another. But this heat is not manifested externally by rise or fall of temperature ; hence it is considered to be hidden in the substance and is called **latent heat.** Thus, if a mixture of ice and water is heated, it is found that the temperature of the mixture remains constant at 0°C until all the ice is melted. Conversely if heat is abstracted from a mixture of ice and water, the temperature does not fall below 0°C until all the water has turned into ice. The heat thus absorbed when a solid melts is known as **latent heat of fusion,** and the heat liberated when a liquid solidifies **latent heat of solidification.** Similarly, when a liquid passes into the vapour state, heat is absorbed without any change of temperature which is called **latent heat of vaporisation** and in the reverse process when a vapour condenses to the liquid state, heat is evolved which is called **latent heat of condensation.**

Sometimes a solid may change directly to the vapour state without passing through the intermediate liquid state. This process is known as **sublimation.** Thus ice and snow evaporate at temperatures below the freezing point and ice is often found with an envelope of vapour around it. The reverse process of a vapour passing directly to the solid state is called **formation of hoar-frost** The aim in this capter is to study the fundamental laws and other peculiarities of the phenomena of fusion, vaporisation and sublimation, and indicate some of the practical applications based on them.

FUSION

1. Melting point. One of the basic laws of fusion is that *while fusion or solidification is taking place the temperature of the mixture remains constant, provided the substance is pure and the external pressure is fixed.* The steady temperature at which a solid melts is called the *melting point* (or fusion point) and the steady temperature at which a liquid solidifies the *freezing point* (or solidification point). *For pure substances, i.e. crystalline* substances such as ice, naphthalene, etc., *the melting and freezing points coincide,* whereas in the case of *amorphous* substances like iron, glass, wax, etc., fusion and solidification take place over a short range of temperature, so that their melting and freezing points are not fixed with definiteness. Since the melting or freezing point varies with different substances, it is often used to differentiate substances. The melting point ordinarily changes little with the external pressure. For instance, to lower the melting point of ice from 0°C to – 1°C, a pressure of about 130 atmospheres is required. It is to be noted that substances may be temporarily cooled to a temperature below the normal freezing point without solidifying, which is known as *supercooling* or *surfusion.*

Determination of melting points of substances.

(*a*) *Cooling curve method* is very reliable if the substances can be had in a reasonable quantity. The substance is taken in a test-tube and heated until it is completely melted and its temperature rises a good bit above the melting point. The melted substance is allowed to cool, protected from air currents, and its temperature is noted at regular intervals of time, say every minute or half-minute, until the temperature falls a little beyond the solidification point. With the data thus obtained if a graph is drawn representing temperature against time, a curve is obtained, known as the *cooling curve*, which is of the form shown in Fig. 71. It is seen that the curve has three parts: AB representing the rapid cooling of the molten substance, BC indicating a constant temperature for a short period of time at which the solid and liquid states of the substance can coexist in equilibrium and CD representing the cooling of the solid substance. At B the substance is entirely in the liquid state, while at C it is entirely in the solid state. Thus the distinction between the liquid and solid states is sharply defined. The constant temperature corresponding to the horizontal portion BC is the melting point of the solid.

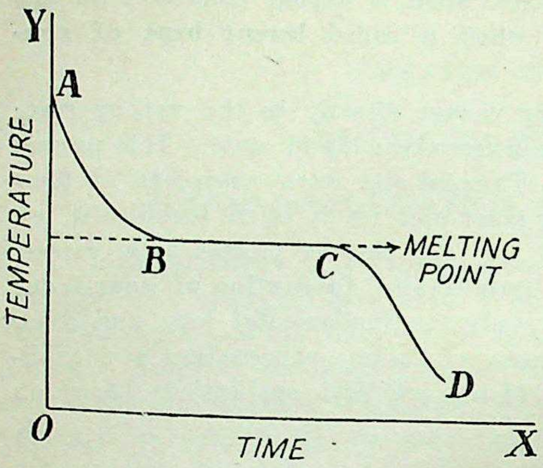


Fig. 71. Cooling curve.

For an amorphous substance, the portion BC will be slightly inclined instead of being horizontal, indicating that there is a finite fall of temperature during the change of state. This discrepancy is attributed to the presence in amorphous substances of two or more crystalline substances which do not solidify at the same temperature, as will be explained below in connection with the fusion of alloys. As a matter of fact, mixtures or even the presence of small impurities affect the sharpness of definition of the melting point. This property is used to test the purity of organic compounds in their preparation.

The above simple method is well adapted for substances, whose melting points are not too high, but limited up to about 100°C, such as ice, naphthalene, wax, etc. If the melting point to be determined is rather high, as in the case of many metals, the apparatus must be suitably modified as follows : The substance must be heated in a crucible of graphite or some other material whose melting point is higher than the substance under test. The heating is done electrically with advantage and in a non-oxidising atmosphere. For measuring temperature a thermocouple thermometer is generally used, taking care to protect the junction inserted in the melting substance with a sheath made of porcelain or hard glass tube. As long as the substance is melting, the temperature remains constant and hence the *e.m f.* of the thermocouple is also stationary. Plotting a graph representing the *e.m.f.* against time, the cooling curve, like the one in Fig. 71, is obtained. The horizontal part of the curve represents the freezing of the substance and the corresponding *e.m f.* gives its melting point.

(*b*) *Method of opacity* is useful for substances, like wax, which are opaque in the solid state and transparent in the liquid state. The substance is heated and the temperature at which the opacity just disappears is noted. When the substance has completely melted, it is cooled and the temperature at which the opacity just sets in is noted. The mean of the two temperatures is taken as the melting point, provided they differ by less than a degree.

If only a small quantity of the substance is available, it is introduced in a short length of capillary tubing which is attached to a thermometer by rubber bands. It is then heated by immersing the thermometer in a suitable hot bath and the temperatures at which it melts and solidifies on cooling again, as indicated by the disappearance and appearance of opacity, are observed. The average of the two temperatures gives the melting point of the substance.

If the substance is not only rare but also has a high melting point, it can be employed in the form of a wire.

Melting point of alloys. Alloys occupy apparently an anomalous position as regards the melting point. Many alloys melt like amorphous solids. They first become pasty or partially liquefied at the melting point of the more easily fusible component and liquefy completely as the melting point of the less fusible component is reached. On cooling the molten alloy, the temperature remains stationary when the melting point of the less fusible component is reached, then it falls gradually and again becomes stationary at the melting point of the more fusible component. Certain alloys, however, have one definite melting point like crystalline solids. They have the peculiar property that their melting point is very much less than that of any of the components. Thus, *Rose's alloy* which consists of 2 parts of bismuth (269°C), 1 part of lead (327°C) and 1 part of tin (232°C) melts at 94°C ; *Wood's alloy* (4 parts of bismuth, 2 parts of lead, 1 part of tin and 1 part of cadmium) melts at 60°C about.

If two metals are mixed together to form an alloy, it is found that *the melting point is not only always less than that of either constituent, but also varies in a regular manner with the composition of the alloy.* For instance, if an alloy containing 10% copper (1083°C) and 90% silver (960°C) is melted and then cooled, it begins to solidify at 880°C, crystals of pure silver separating out, thus making the residual liquid richer in copper. At the same time the freezing point of the residual liquid decreases and the temperature continues to fall. When an alloy containing 30% of copper and 70% of silver is studied in a similar manner, solidification starts at 770°C, crystals of pure silver separating out. This continues until the temperature has fallen to 740°C, when the whole alloy freezes. This solid consists of 40% of copper and 60% of silver and is known as an *eutectic alloy* and its freezing point as the *eutectic point,* which is the lowest temperature at which the alloy can melt. In more complex alloys there is more than one eutectic point.

The fact that the addition of one metal to another causes a lowering of the melting point resembles the effect of a solute on the freezing point of the pure solvent, (which we shall consider below) and hence suggests that the liquid alloy may be considered as a solution of one metal in the other.

Two interesting practical applications of the melting point of an alloy being lower than that of any of its constituents are :—(*i*) The addition of "flux" to a substance of high melting point in order to melt it more easily. (*ii*) In the production of metals by electrolysis, the ore is made more readily fusible by adding another compound of the same metal.

Freezing point of solutions. *Solutions in water or other liquids have a lower freezing point than that of the pure solvent.* When for instance salt is added to pure water, it lowers the freezing point to an extent proportional to the concentration, the freezing point of a saturated solution being −23°C about. It may be noted here that solids may be changed into the liquid state not only by heating them (*i.e.*, by *fusion*), but also by dissolving them in a solvent (*i.e.*, by *solution*). The salt, when dissolved in water, changes its state, for which it requires heat (*i.e.*, its latent heat) ; it takes this heat from the solution and the temperature is lowered. When a salt solution is cooled, pure ice separates out at the freezing point depending on the initial concentration just as one of the pure metals crystallises out in the case of an alloy. The residual solution gets more and more concentrated and hence has a lower and lower freezing point, until at about – 23°C, the solution is saturated and a solid mixture of salt and ice with 23·6% salt is formed, which is known as a *cyrohydrate.* It is like the eutectic alloy and the minimum temperature corresponds to the eutectic point.

The effect of solution on the freezing point has a great importance in the theory of solutions. For fairly dilute solutions *the depression of the freezing point of the solution is directly proportional to the concentration and inversely proportional to the molecular weight of the solute.* The depression produced when one gram molecule of a solute is dissolved in 100 grams of water is known as the *molecular or molar depression of the freezing point* of the solution. In the case of *non-electrolytes*, such as sugar, tartaric acid, etc., the molar depression has a constant value of about 18·3°C. For *electrolytes,* like sodium chloride, hydrochloric acid, etc. the molar depression is also constant, but has a value of 36·2°C, roughly double the value for non-electrolytes, which is accounted for by the dissociation of electrolytes in solution. Arrhenius has used these facts as evidence for the dissociation theory of electrolytic conduction.

Beckmann's apparatus for the determination of the freezing point of solutions. Beckmann has devised a method of measuring the freezing point of solutions with great accuracy. The apparatus consists of a test tube A closed with a cork through which a Beckmann thermometer T and a platinum stirrer P are inserted. The test tube is enclosed in an air-jacket B. The solution whose freezing point is to be determined is poured into the test tube through a side-tube C. The test tube is placed in a bath of a suitable freezing mixture, provided with a stirrer S. (Fig. 72).

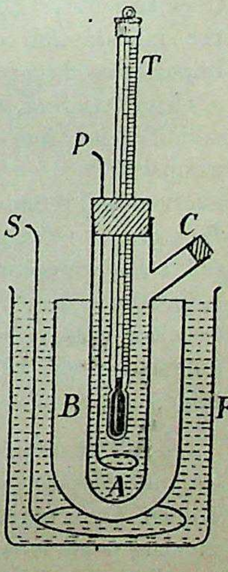


Fig. 72. Beckmann's freezing point apparatus.

The solution is first supercooled to a few degrees below the approximate freezing point by stirring the freezing mixture and allowing the apparatus to stand undisturbed. The solution is then stirred well with the platinum stirrer, when its temperature rises, reaching a value, where it remains constant for some time. This constant temperature, noted by the sensitive thermometer T, gives the freezing point of the solution, as we shall see presently. Beckmann with his apparatus was able to establish the different effects produced on the freezing point by solution, such as the lowering of the freezing point, direct proportionality between depression of freezing point and concentration, the constancy of molar depression both in the case of electrolytes and non-electrolytes, etc.

Supercooling or surfusion. Most liquids, if cooled in a pure state in a perfectly clean vessel, with least disturbance, can be lowered to a temperature much below the normal freezing point, without solidifying. This is known as *supercooling* or *surfusion.* Thus, if a test tube of distilled water is cooled slowly without stirring the water, the temperature is found to fall 3 or 4 degrees below 0°C without any ice being formed. Water can be cooled in this way even up to − 10°C with a little care, and up to − 12°C when covered with a layer of oil. Dufour supercooled a drop of water to as low as − 20°C by surrounding it with a liquid of the same density but lower freezing point. Naphthalene, sulphur, phosphorus, antimony, etc., have also been supercooled far below their normal solidification points.

The phenomenon of supercooling does not really go counter to the fact that a liquid solidifies at a definite temperature, which is its freezing point. For it is essentially an *unstable phenomenon,* since the introduction of the smallest quantity of the solid or even of impurity as dust particles, or any mechanical disturbances, such as shaking, stirring, etc. is enough to start solidification. When once the solidification has started, the liquid continues to solidify and its temperature rises to the normal freezing point with the latent heat evolved and remains there until the entire mass has solidified. This fact, *viz.* the temperature of a supercooled liquid rises to freezing point and remains constant for some time as soon as solidification commences, has been utilised in Beckmann's determination of the freezing point of solutions. An adequate explanation of the phenomenon on the basis of James Thomson's hypothesis will be given later.

Effect of pressure on melting point. As already mentioned, the melting point of a substance changes when the pressure is varied. Hence, strictly speaking, the pressure must be specified when a melting point is started. A theoretical relation between the increase in pressure and the change in the melting point known as the *Clausius*

Clapeyron relation can be derived on the basis of thermodynamics as we shall see later. It is of the form

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$$

where v_2 and v_1 are the specific volumes of the liquid and solid respectively at temperature T, dp/dT the ratio of the change of pressure with the change of the freezing point and L the latent heat of fusion.

From this relation it can be readily deduced that *the melting point of a few substances, which increase in volume on solidification,* (*or contract on melting*) like ice, iron, antimony, etc., *is lowered by increase of pressure,* whereas, *the melting point of most substances, which contract on solidification* (*or expand on melting*) *like wax, copper, etc. is raised by increase of pressure.* Calculation shows that in the case of *ice* the melting point is lowered by about 0·0073°C per atmosphere increase of pressure, whereas in the case of *paraffin wax,* the melting point increases by about 0·04°C per atmosphere.

These theoretical predictions were first tested, in 1850, by Lord Kelvin in the case of ice by an ingenious apparatus and found to be true. But very accurate experiments were carried out in 1880 by Dewar, who measured the melting point of ice at various pressures up to 700 atmospheres. His apparatus (Fig. 73) consisted of an iron bottle A filled with a mixture of ice and air-free distilled water and closed by a tight screw D. The bottle could be put in communication with a pump and manometer. The temperature of the contents of the bottle were measured accurately with a thermocouple C, one junction of which was inserted in the mixture while the other was kept at a fixed temperature by immersing it in melting ice. The bottle was completely immersed in a bath of melting ice B.

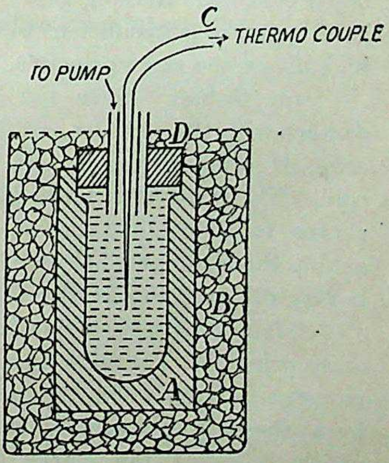


Fig. 73. Dewar's apparatus.

The pressure on the mixture inside A was increased by steps of 25 atmospheres and the temperature of the mixture, when steady, was observed with the thermocouple. Dewar found that the melting point of ice decreased with increase of pressure regularly up to 700 atmospheres at the mean rate of 0·0072°C per atmosphere.

Familiar examples of the lowering of the melting point of ice with increase of pressure are :—

(*a*) *Regelation*, discovered by Faraday and elegantly demonstrated by Tyndall by the following simple experiment. When a piece of wire loaded at both ends with equal weights is slung across a block of ice it is found that the wire cuts its way through the ice without however dividing the block into two pieces. The reason is that due to the pressure the ice immediately below the wire melts which enables the wire to sink through ; but once the pressure is released, the water above the wire solidifies into ice again. It may be noted that the latent heat required to melt the ice below the wire comes from that evolved by the water solidifying above it. Hence, a copper wire will cut through the ice more quickly than an iron wire, because copper is a better conductor than iron.

(*b*) *Snowballs* can be made by pressing fresh snow with hands. The small pressure applied is sufficient to melt particles of snow inside and removal of pressure binds the particles of snow into a stable form of a ball. If, however, the temperature of the snow is much below the freezing point, such balls cannot be formed, since the hand pressure is insufficient to cause melting. Figures in snow can be built on the same principle.

(*c*) *Skating*. Since the edges of the skates, which are first in contact with the solid ice, are fine, the pressure, *i.e.*, force per unit area, is ordinarily sufficient to melt momentarily the ice, however cold. The water thus formed acts as a lubricant and enables the skates to glide along the ice. The edges usually sink far enough to enable them to "grip" the ice, which would not be possible if the ice is very cold and this is why skates do not "bite" in very cold weather.

(*d*) *Glacier motion* also has received a partial explanation on the same principle. As snow goes on accumulating on a mountain, a moment arrives when the mass attains sufficient weight to melt the ice at the bottom layers under pressure ; then a huge mountain of ice which is called the glacier, gradually slips down the slopes of the mountain, the melted layers resolidifying with the release of pressure.

(*e*) *Metal casting*. An important practical application of metals that expand on solidification is made in metal casting. In order to obtain sharp casts from a mould, iron which expands on solidification is used ; casting in copper or silver is much less sharp, since these metals contract on solidification.

2. Latent heat of fusion. A second important feature of fusion is the latent heat involved in the process. As already mentioned, during fusion heat is absorbed by the substance and an equal amount of heat is evolved by the substance during solidification, without any external manifestation as rise or fall of temperature of the substance. This 'hidden' or 'latent' heat is explained as follows: In a solid, the molecules vibrate about mean equilibrium positions which are fixed, but in a liquid they execute rotational and translational motions and wander about, though considerably hampered by mutual influence. In order to endow the molecules with these extra motions and also to overcome the forces which held them confined in the solid state work must be done and this work is the equivalent of the latent heat of fusion. Later, we shall show that latent heat is necessary to supply the *internal work* required to separate the molecules against their mutual attraction and the *external work* done by change in volume of the substance.

The *latent heat of fusion* is defined as *the quantity of heat in calories, required to convert 1 gram of the solid at its melting point into liquid at the same temperature.* The *latent heat of solidification* is evidently equal to the latent heat of fusion and is defined in a similar manner.

In the following table, the latent heats of fusion of some solids are given, which will enable us to realise their magnitude.

Substance	*Latent heat of fusion* (*cals.* /*gm.*)
Aluminium	92·4
Ice	79·6
Copper	43·0
Naphthalene	35·6
Paraffin wax	35·0
Zinc	26·6
Silver	22·0
Tin	14·6
Sulphur	9·4
Lead	5·4

It is seen that a good amount of heat is absorbed when ice melts. It is well that it is so. If the latent heat of fusion of ice were small, snow and ice would melt very rapidly in summer causing disastrous floods; ponds and lakes would freeze much too quickly in winter, destroying fish and other life in them; the distribution of glaciers would change, so that portions of earth's surface which are now permanently covered with ice throughout the year would be completely cleared for a part of the year.

Determination of the latent heat of fusion. (*i*) **The method of mixtures,** already described in connection with the determination of specific heat, provides a simple and accurate way of finding the latent heat of fusion of ice. A calorimeter containing W grams of water is taken, the initial temperature of water θ_1 is noted and m grams of dry ice at 0°C are added, taking care that too much ice is not used, so that the final temperature may be well above the dew point of the atmosphere, since otherwise the atmospheric moisture will condense on the calorimeter. The calorimeter and contents are stirred until all the ice has melted and the final temperature θ_2 is observed. If L is the latent heat of fusion of ice, we have

$$m\,\mathrm{L} + m\,\theta_2 = (\mathrm{W} + w)\,(\theta_1 - \theta_2)$$

where w is the water equivalent of the calorimeter.

An *important source of error* is due to some water adhering to bits of ice at 0°C. To eliminate this, ice below 0°C is often used, in which case an additional term has to be added to the left hand side of the above relation, taking into account the heat required to warm the ice to 0°C. This requires a knowledge of the specific heat of ice, which is much less than that of water.

Radiation correction has to be applied as usual. In the case of ice, the correction can be conveniently eliminated by adjusting the initial temperature of the water to be as far above the room temperature as the final temperature is expected to be below it, so that the loss of heat in the first half of the experiment is about equal to the gain of heat of the second half. But in other cases, Barton's method of correction is most suited. It is to be noted that in the present case, the temperature-time curve will be of the form shown in Fig. 74. But the correction $\delta t'$ is, however, given by the usual relation

$$\delta t' = \frac{\text{area ABE}}{\text{area EBCF}} \times \delta t.$$

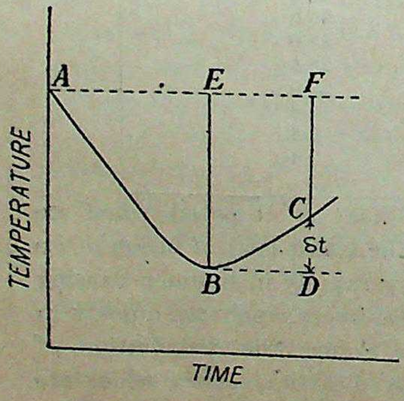


Fig. 74.

This correction is evidently to be *subtracted* from the actually observed final temperature, in order to get the corrected final temperature $(\theta_2 - \delta t')$.

The method of mixtures has been employed by Goodwin and Kalmus to determine simultaneously the latent heat of fusion and the melting point of metals and their salts with the following modifications. A known mass of the substance is enclosed in a sealed water-tight cylindrical platinum vessel and heated in an electric furnace, which is specially designed to secure a uniform high temperature over the entire cylinder. A Pt-Rh thermocouple is used to measure accurately the temperature of the platinum vessel and contents. The substance, having thus been raised to any desired high temperature, is dropped into a calorimeter containing water (or aniline for temperatures above 400°C) and the quantity of heat liberated is determined, in the usual manner by noting the final temperature of the calorimeter and contents.

The thermal capacity of the empty platinum vessel is first determined by a preliminary experiment. Then using the substance the experiment is performed with different initial temperatures ranging from about 50°C above to 50°C below the melting point. From the experimental data, the amount of heat H required to raise 1 gram of the substance from the room temperature to the initial temperature is calculated. Plotting H against the initial temperature T curves of the type shown in Fig. 75 are obtained. The latent heat of fusion is given by the discontinuity in the value of H represented by the vertical line. The melting point is given by the temperature at which the discontinuity appears. The slope of the curve at any temperature gives the specific heat of the substance at that temperature.

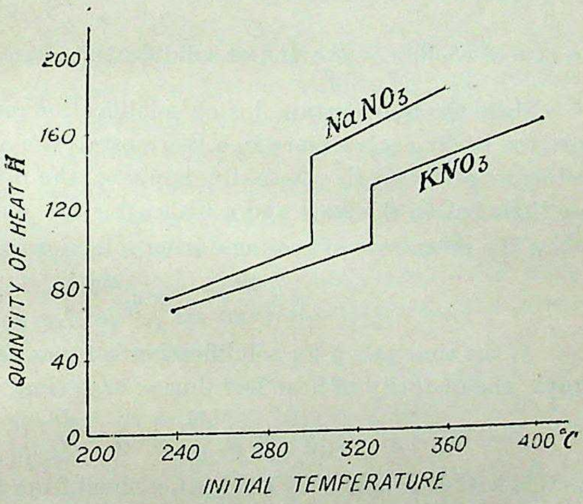


Fig. 75.

(*ii*) **The method of cooling** offers a convenient way of determining the latent heat of fusion of solids of low melting points. The substance is placed in a light calorimeter of low thermal capacity and heated until it completely melts and its temperature rises to about 10°C above the melting point. The calorimeter and content are then suspended inside a thermostat; the molten substance is kept gently stirred and its temperature noted with a sensitive thermometer at regular intervals until it completely solidifies and drops in temperature to about 10°C below the melting point. A graph is drawn with temperature against time to obtain the cooling curve, which will be of the form shown in Fig. 71 (*Cf.* p. 174). From this curve the rates of fall of temperature $\frac{d\theta_1}{dt}$ and $\frac{d\theta_2}{dt}$ at the *beginning and end of solidification* respectively can be obtained.

Now if m be the mass of the substance used, s_1 and s_2 its specific heats in the liquid and solid states,

the rate of cooling at the commencement of solidification $= m\ s_1 \frac{d\theta_1}{dt}$

the rate of cooling at the end of solidification $= m\ s_2 \frac{d\theta_2}{dt}$.

Since the temperature during solidification remains constant and since the cooling takes place in a thermostat, the above two rates of cooling must be equal. Actually, however, the rates of cooling refer to a little before the start and a little after the end of solidification. Hence the mean rate of cooling during solidification can be taken as

$$\tfrac{1}{2}\left(m\ s_1 \frac{d\theta_1}{dt} + m\ s_2 \frac{d\theta_2}{dt} \right)$$

If the time taken for solidification is t secs., as indicated by the graph, the quantity of heat lost during that time

$$= \tfrac{1}{2}\left(m\ s_1 \frac{d\theta_1}{dt} + m\ s_2 \frac{d\theta_2}{dt} \right) t$$

As this heat is supplied by the heat evolved from the substance during solidification

$$m\,\mathrm{L} = \tfrac{1}{2}\, m\, t \left(s_1 \frac{d\theta_1}{dt} + s_2 \frac{d\theta_2}{dt} \right)$$

Or $$\mathrm{L} = \tfrac{1}{2}\, t \left(s_1 \frac{d\theta_1}{dt} + s_2 \frac{d\theta_2}{dt} \right)$$

from which L can be estimated, provided the specific heats of the substance in the liquid and solid states, *i.e.*, s_1 and s_2 are known.

3. Change of properties on melting. When a substance melts, several of its properties change in a marked manner, due evidently to the regular and compact arrangement of the molecules in the solid state giving place to the more irregular and more free movement of the molecules in the liquid state under the influence of heat. We shall here consider only a few important properties that undergo such changes :—

(*a*) *Change of volume.* The effect is common to both crystalline and amorphous solids. Several solids, such as ice, iron, bismuth, animony, etc., contract on melting and expand on solidifying. It has been experimentally found that ten parts in volume of water at 0°C expand to eleven parts in volume of ice on solidification. As we have already seen, this expansion is the source of a very great force which causes water pipes to burst in frosty weather, rocks to split, etc., but it has also been utilised with advantage for good castings ; it may be mentioned in this connection that alloys of lead and bismuth or of lead, copper and antimony are used as *type metals*, since they expand on solidifying and thereby fill up all the minute lines and crevices in the moulds, which are therefore reproduced with great exactness.

But most substances, like the majority of metals, paraffin wax, etc., expand on melting and contract on solidifying. A number of experiments have been carried out to determine directly the volume of liquid formed from a given volume of the solid. But a simpler and more accurate method of measuring this change of volume is to determine the densities of the solid and liquid at the melting point.

(*b*) *Change of electrical resistance.* When metals are melted, they undergo a sudden change in their resistance. If the metal is one which expands on melting, its resistance increases, if it contracts on melting, its resistance decreases.

(*c*) *Atomic latent heat. Trouton's rule.* The product of the latent heat of fusion and the atomic weight of a substance is known as the *atomic latent heat*. The ratio of the atomic latent heat (A × L) to the melting point (T_m) in absolute scale has been found to be approximately constant for all substances, which is called the *Trouton's rule*. The value of the constant seems to depend upon the crystal system in which the substance solidifies, as seen from the following table :—

Substance	*Atomic latent heat* (A × L)	*Melting point* (T_m)	$\frac{AL}{T_m}$	*Crystal system*
Na	630	371	1·7	Space-centred cube
K	570	336	1·7	
Rb	520	312	1 7	
Cs	510	300	1·7	
Bb	1170	600	1·95	Body-centred cube
Al	2500	930	2·69	
Ag	2630	1234	2·13	
Cu	2750	1356	2·03	
Au	3100	1336	3·32	

VAPORISATION

1. General remarks. The following general remarks, will be found useful for a proper understanding of the phenomenon of vaporisation.

(*a*) *Two methods of vaporisation.* The passage of a substance from the liquid to the vapour state can take place in two ways, *viz.*, (*i*) **evaporation** in which there is a *slow* formation of vapour *at all temperatures* and from *only the free surface of the liquid* and (*ii*) **ebullition** or **boiling,** in which there is a rapid formation of vapour *from all parts of the liquid* as indicated by visible bubbles, and at a *constant temperature* known as the *boiling point*, under nomal conditions of purity of the liquid and external pressure. Hence in dealing with the change from liquid to vapour we have to consider not only the rapid change at the boiling point but also the slower change which goes on at all temperatures.

The phenomenon of *evaporation* is well known : a liquid left exposed to air slowly disappears ; although this evaporation goes on at all temperatures, its rate increases with rise of temperature, since, for instance, a dish of water disappears faster during hot summer than during cold winter ; some liquids, like ether, alcohol, etc., evaporate more quickly than others, like water, oil, etc. Vaporisation by *boiling* is also a fact of common experience. When, for instance, water is boiled, steam is given off, and the amount of water steadily diminishes and finally disappears, the whole process taking place without any change of temperature ; a large increase in volume is also noted when water is changed into steam. It is to be noted that evaporation resembles boiling in many respects, since it involves no change in temperature, and is accompanied by an absorption of heat (latent heat) and a change of volume ; but it differs from it in that it can take place at any temperature, while boiling takes place at a definite temperature under a given pressure.

(*b*) *Vapour pressure.* The vapour, thus formed in evaporation or in boiling resembles a gas and exerts pressure in the same way as a gas does. Simple experiments, conducted, for instance, by introducing liquids in the closed space above the mercury column in a barometer tube, show that :—

(*i*) The vapours of different liquids exert different pressures at the same temperature.

(*ii*) For a given liquid, the vapour pressure steadily increases and reaches a maximum value, which is known as the *saturated* *vapour pressure*, provided the existing conditions of amount of liquid available and of temperature are favourable ; a vapour in equilibrium in the presence of its liquid is bound to be saturated.

(*iii*) The saturated vapour pressure has a definite value at a given temperature, and increases as the temperature rises ; but it is entirely independent of the volume occupied.

(*iv*) The pressure exerted by the vapour before it reaches the saturation stage is known as *unsaturated vapour pressure*, which depends both on the volume and the temperature and is found to obey *Boyle's law* accurate to about 2%, the deviation getting more marked as the pressure increases. A vapour in the absence of its liquid is likely to be unsaturated. *Super-heated* vapour, *i.e.*, saturated vapour whose temperature is increased under constant pressure becomes unsaturated. The various characteristics of vapour and the pressure exerted by it will be dealt with in detail in a later section.

(*c*) *Explanation of the phenomenon of vaporisation.* The mechanism involved in the change of a liquid to vapour can be understood in a simple manner as follows :—

In a liquid the molecules move about amongst themselves in such a way that they are influenced to a great extent by each other ; they cannot travel any appreciable distance without encountering others and having their directions of motion altered either by impact or mutual influence ; in other words, there is *no free-path* for the molecules in a liquid. *In a gas* or vapour, the molecules move about much more freely having *a free-path* between collisions when they are very little influenced by each other. In the passage of a liquid into the gaseous state, the molecules must be first liberated from their mutual influence and the work done for this purpose represents part, at least, of what is known as *the latent heat of vaporisation*.

In the interior of a liquid, each molecule is constantly under the attractive influence of those which surround it and it will experience more or less the same force in all directions, so the path travelled by it will depend on chance collision with the others. *At the surface of the liquid*, however, conditions are very different. A molecule on the surface is not surrounded on all sides by other molecules, so that it will experience a resultant force of attraction towards the interior of the liquid. Thus the surface layer exerts a pressure on the liquid underneath and acts like an elastic membrane stretched over the surface, which explains the hydrostatic phenomenon of *surface tension*.

During *evaporation*, the molecules on the surface of the liquid acquire sufficient velocity to overcome the above mentioned pull towards the interior and escape into the *open space* above the liquid, to get mixed up with the air molecules, but never more to return to the liquid. These molecules constitute the vapour of the liquid. Since the molecular agitation depends on the temperature, the velocity of the molecules increasing with increase of temperature, the rate of evaporation will depend on the temperature.

If evaporation takes place *in a closed space*, some of the vapour molecules after wandering about in the enclosure may strike the surface of the liquid and be drawn into it ; in the meanwhile others will be leaving the surface. As the closed space cannot contain more than a certain maximum number of molecules, a stage will soon be reached when as many molecules return to the liquid as leave it, and an equilibrium state is attained, which is possible only if there is always a sufficient quantity of the liquid. Under these conditions the closed space above the liquid will have its maximum quota of molecules and is said to be *saturated* with the vapour of the liquid and the pressure exerted by the vapour in the enclosure is the *saturated vapour pressure* at the temperature of the enclosure and liquid.

If, however, sufficient liquid is not present, as evaporation continues more molecules will leave the liquid than return to it, until all the liquid disappears. Or, even if there is enough liquid, the enclosure above it may not contain the maximum number of molecules it could. Under these conditions, the closed space above the liquid is said to be *unsaturated* with the vapour and the pressure exerted by the vapour in it is the *unsaturated vapour pressure*.

When a liquid is steadily heated, the velocity of the molecules increases, and a greater number of molecules acquire the velocity necessary to escape from the liquid surface, so that the escape of vapour at the surface becomes marked. After a while, when the surface of the liquid is unable to afford the means of sufficiently rapid escape of the vapour, bubbles of vapour begin to appear at numerous points on the walls of the containing vessel but not in the body of the liquid. They are formed by the evaporation of the liquid into small bubbles of air clinging to the bottom and sides of the containing vessel. When the temperature of the liquid is below the boiling point, the bubbles cannot increase in size since the sum of the pressures of the vapour and the air in the bubbles is less than the hydrostatic pressure due to the atmosphere and the liquid. As the temperature rises, a point is reached, due to the rapid increase of vapour pressure with temperature, when the total pressure inside the bubbles is equal to or just exceeds, the external pressure. The bubbles will now grow, and with further evaporation they will become too big and buoyant to remain attached to the sides. They then break away and rise to the surface in quick succession. The occluded air which is present in the walls of any vessel keeps up the initial formation of bubbles. The rapid escape of the bubbles through the mass of the liquid causes the latter to be agitated, which is then said to *boil.* If the heating is continued further it is found that the temperature of the liquid remains stationary. Only bubbles are formed more rapidly to keep the balance between their loss and supply. The temperature at which this occurs is the *boiling point.* Since vaporisation occurs in this process through bubble formation, it is called *ebullition* or *boiling.* Thus we see that boiling can occur only at a definite steady temperature at which the maximum vapour pressure of the liquid is equal to the external pressure.

If the boiling is continued for some time, it will be noticed that the bubbles are getting smaller and less frequent and the temperature rises above the boiling point, by quite a good amount when the vessel is very clean and smooth. After a time the boiling ceases altogether. This is known as *superheating.* Then a few large bubbles are produced explosively and the liquid is quiet again for some time. This process is repeated at intervals and is known as *delayed boiling* or *boiling by bumping.* These phenomena will be accounted for in a later section.

2. Evaporation. The characteristic feature of this process of vaporisation, is that it *may occur at any temperature* and is a *surface effect,* as already stated. The sole factor governing it is the state of the air in the neighbourhood of the liquid : if the air is saturated or nearly so, as on a "calm, damp" day, evaporation hardly takes place ; if, on the other hand, the air is unsaturated as on a "dry, windy" day, evaporation is greatly promoted. Similarly bubbling air through the liquid will cause rapid evaporation, since each bubble exposes a large surface to the liquid (evaporation being a surface effect) and is then swept away. It may be noted that the oppressiveness of a moist humid heat is due to the saturation of the air retarding or stopping the evaporation of perspiration which is the Nature's way of keeping the body cool at a uniform temperature.

Other conditions that help evaporation are :—

(*i*) the liquid should have a *low boiling point, i.e.,* be a *volatile liquid*. Since at the boiling point the vapour pressure of the liquid is equal to the external atmospheric pressure, the lower the boiling point, the greater will be the vapour pressure at ordinary temperatures. Hence ether (B.P. 35°C) evaporates more quickly than alcohol (B.P. 78°C) and alcohol more quickly than water (B.P. 100°C) at the room temperature ;

(*ii*) the liquid and surrounding air should have *high temperature*. The higher the temperature of the liquid the greater the pressure exerted by the escaping vapour, and the higher the temperature of the air the greater the quantity of vapour it will contain before saturation is reached ;

(*iii*) the *atmospheric pressure should be low,* since a low external pressure helps the escape of vapour from the surface.

Cooling due to evaporation. When a liquid evaporates, it requires heat for changing from the liquid to the vapour state (latent heat of vaporisation). If there is no supply of heat, the liquid will draw the necessary latent heat from its surroundings and thereby cool itself. Under favourable conditions even intense cooling can be produced in evaporation, which finds a very useful application in certain types of ice machines, as we shall see later. Some of the familiar examples of cooling caused by evaporation are :—(*i*) During summer water is kept in porous pots and exposed to a draught, in order to have it cool ; some water passes through the pores to the outside, evaporates fairly quickly due to the current of air and produces cooling. (*ii*) Vessel may likewise be kept cool by wrapping them in damp cloth and placing them in a draught. (*iii*) Evaporation of the perspiration from our bodies helps to keep us cool, as already stated. (*iv*) The unpleasant, intense and even dangerous chill experienced after getting wet through. This is due to the fact that the large amount of latent heat, required by the water as it evaporates from the wet clothes, is drawn from the body. (*v*) In summer, sprinkling the floors and screens with water produces a cooling effect by evaporation.

3. Boiling point. As already mentioned, the chief characteristic feature of vaporisation by boiling is that it takes place at *a definite temperature* called the *boiling point,* under the actual conditions of the experiment. Since it has been shown that boiling can occur only at the temperature at which the saturated vapour pressure of the liquid is equal to the external pressure acting on the liquid, the *boiling point of a liquid may be defined as the temperature at which its saturated vapour pressure is equal to the external pressure acting on it, i.e., the atmospheric pressure.* Thus under normal atmospheric pressure of the 760 mm. the boiling point of water is 100°C, of aniline 184·2°C, of kerosene 240°C, of mercury 356·7°C, of alcohol, 78·3°C, of ether 34 6°C and so on.

Determination of the boiling point of a liquid. Utilising the principle stated above in the definition of the boiling point this quantity for any liquid can be experimentally determined as follows. A glass, thick-walled J-tube, the shorter limb of which is sealed, while the longer one is open, is used. Sufficient quantity of the liquid is enclosed in the shorter limb by a column of mercury, as shown in Fig 76. The tube is placed in a liquid bath whose boiling point is higher than that of the liquid under study. As the bath is steadily heated, the enclosed liquid is gradually changed to its vapour ; the pressure exerted by this vapour pushes down the mercury column in the closed limb. After a time the mercury levels in the two limbs will become equal, showing that the saturated vapour pressure of the liquid is equal to the external atmospheric pressure. The temperature of the bath at this stage is noted with a sensitive thermometer. As the bath is further heated, the level of the mercury in the open limb will become higher than that in the closed limb, thereby indicating that the saturated vapour pressure increases with temperature and exceeds that of the atmosphere. Allowing the bath to cool, its temperature is again observed when the levels in the two limbs are the same again. The mean of the two temperatures gives the boiling point of the liquid. This method is well suited even for liquids which are available only in small quantities.

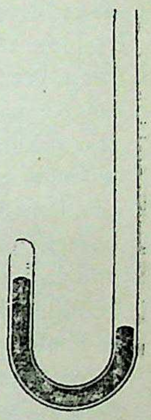


Fig. 76.
Boiling point of a liquid.

Superheating. Under certain conditions, a liquid can be heated much above its boiling point without boiling taking place. It can be observed, for instance, when water free from dissolved air is carefully heated in a vessel which has been specially cleaned to remove all dust, grease and occluded gas. It is found that in such a case the temperature of the water can be raised up to 137°C without boiling; but when boiling starts due to any kind of disturbance, it is of an explosive nature, ordinarily called *bumping*, and the temperature falls to 100°C. Dufour has been able to heat a bubble of air-free water to 178°C by enclosing it in a mixture of oils of high boiling points but of the same density as water.

Like supercooling, superheating also is *an unstable phenomenon.* Since it is always accompanied by boiling by bumping, its explanation must be sought for in the study of the latter phenomenon.

Boiling by bumping. As already noted, this phenomenon, which follows superheating, is intermittent and violent in nature. It is called *bumping* on account of the bumping noise made by the whole body of the liquid falling back to the bottom of the vessel after having been lifted up by a few large bubbles. It can be suppressed by placing in the vessel some porous objects, such as bits of porcelain, sand, etc., when the boiling at once becomes quiet and regular and the temperature resumes its normal value. This fact combined with the other, *viz.*, superheating takes place only under conditions of extreme purity of both the vessel and the liquid, shows that the two phenomena are *due to the absence of nuclei such as dust particles, impurities or bubbles of gas.* For, if there are no nuclei around which the vapour molecules can collect to form bubbles, the radius of any bubble they form by themselves must be very small. As the liquid is heated to the boiling point, such small bubbles of vapour cannot persist but disappear soon, since their vapour pressure is far too small to counteract the pressure due to surface tension (which varies inversely as the radius : $p = 2T/r$) and the hydrostatic pressure. The liquid has therefore to be heated much above the boiling point in order to make the vapour pressure of these small bubbles equal to the sum of the pressure of surface tension and the hydrostatic pressure. This explains superheating. When the above condition is realised, the small bubbles, with a sufficiently high vapour pressure now, begin to grow to cause ebullition, but they do so with explosive violence, since the equilibrium is unstable.

As the bubbles grow, the vapour pressure remains more or less constant since the evaporation is able to keep pace with the increasing surface of the bubbles, provided heat is supplied fast enough ; but with increasing radius, the external pressure due to surface tension decreases and hence the excess of the internal over the external pressure increases rapidly causing the bubbles to burst violently and intermittently. Thus boiling by bumping is explained.

If, on the other hand, nuclei are present, the bubbles of vapour initially formed round them will be larger in size, so that their vapour pressure may easily support the pressure due to surface tension and the hydrostatic pressure. When liquids are heated in ordinary vessels, there are always nuclei present, in the shape of dust particles or impurities which help bubble formation and ebullition sets in at the normal boiling point. Prevention of boiling by bumping by the addition of porous objects which supply the necessary nuclei is also readily understood.

Boiling point of solutions. Similar to the case of freezing point of solutions, the boiling point also is affected by the process of solution. *The boiling point of a solution is higher than that of the pure solvent.* This can be accounted for as follows :—

Solutions obey the same law of boiling as pure liquids, *viz.*, the saturated vapour pressure of the liquid at its boiling point is equal to the atmospheric pressure ; but there is an important difference, *viz.*, *the vapour pressure of a solution at a given temperature is always less than that of a pure solvent at the same temperature.* Thus the vapour pressure of a salt solution at 100°C is less than 760 mm. ; hence the salt solution has to be heated to a temperature higher than 100°C for its vapour pressure to reach the value of the atmospheric pressure, when boiling will set in.

The elevation of the boiling point of a solution is directly proportional to the concentration and inversely proportional to the molecular weight of the solute, as in the case of the depression of the freezing point. The *molar elevation of the boiling point, i e.,* when one gram-molecule of the solute is dissolved in 100 grams of water, is found to be a constant both for non-electrolytes and electrolytes, being 5° and 10° about respectively, hence the latter being about double the former, for the same reasons as given in connection with the freezing point of solutions and hence supporting Arrhenius' theory of electrolytic dissociation in the same way (*Cf.* p. 177).

Beckmann's apparatus for the determination of boiling point of solutions. Beckmann has also designed a special form of boiling point apparatus for solutions, similar to the one for measuring freezing points of solutions. It consists of a test-tube A (to contain the solution whose boiling point is to be determined) fused into a wider glass vessel B (to serve as a boiler). The mouth of A is closed with a cork, through which a Beckmann thermometer T can be inserted to read the temperature of the solution. Both the test-tube and the boiler have side-tubes carrying spiral condensers C_1 and C_2 in order to prevent losses of the liquids through evaporation. (Fig. 77). The given solution is placed in the test-tube. The boiler contains a solution with a boiling point higher than that of the solution studied. It is seen that the bulb of the thermometer is immersed in the solution. Some bits of porcelain or small earthenware balls are introduced both in A and B to help free boiling. The thermometer is usually set at the boiling point of the pure solvent before using it with the given solution, so that the elevation of the boiling point caused by dissolving a known amount of the solute in the pure solvent may be directly read on it in the experiment. From this data, the boiling point of the solution can be calculated, and its variation with concentration, etc., can be studied.

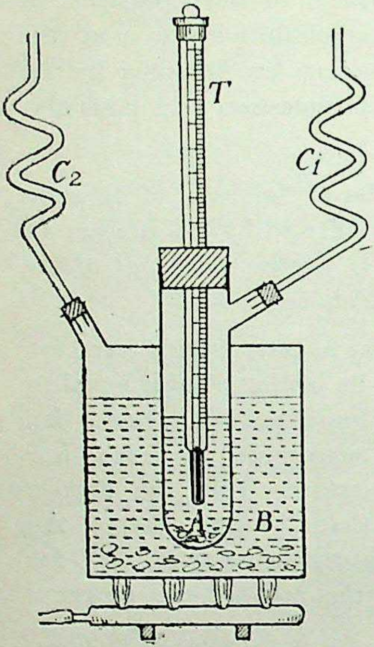


Fig. 77. Beckmann's apparatus for boiling point of solutions.

Effect of pressure on boiling point. From what has been said about the vapour pressure of a liquid at its boiling point, it follows that if the external pressure on the liquid is altered, the liquid will boil at a different temperature at which the vapour pressure will be equal to the new external pressure. Hence also *an increase of pressure raises the boiling point of a liquid and a decrease lowers it.* The Clausius-Claperyron thermodynamical relation given on page 179 can be used to study the variation of boiling point with pressure as in the case of the melting point, as we shall see later.

The effect of pressure on the boiling point is found to be very great, much more marked than on the melting point. Thus, while a pressure of 130 atmospheres are required to lower the freezing point of water by 1°C, a pressure of about 16 atmospheres is enough to raise the boiling point of water by 100°C.

The effect on the boiling point when the external pressure is reduced may be demonstrated by the following simple experiment. Some water is boiled in a flask until all the air is expelled. The flask is then closed tightly and cooled under a stream of cold water, in an inverted position. After a time the water begins to boil, because the pressure over the water has been greatly reduced by the condensation of the steam in the space above the water. It is possible in this manner to make water boil at a temperature as low as 40°C. Evidently the water will not boil for a long time, as the steam evolved soon raises the pressure to a value above the vapour pressure of water at that temperature of boiling.

The relation between the external-pressure and the boiling point can be studied in a more exact and quantitative manner as follows. A suitable apparatus, shown in Fig. 78, consists of a flask A which is connected through a condenser C to a larger flask B, which is put in communication with a mercury manometer M and a pump. The liquid under study, say water, is boiled in A and the boiling point is measured by a sensitive thermometer T, whose bulb is not immersed in the liquid but is just above it, so that the temperature of the vapour rather than that of the boiling liquid is measured, since the latter is affected by the presence of impurities and the nature of the container. The vapour produced during boiling is condensed by C and the condensed liquid runs back to A, thereby not only preventing waste of the liquid but also stopping the pressure from increasing due to the accumulation of vapour. The larger flask B is kept in a bath of cold water and its purpose is to keep the pressure constant by damping out small variations in pressure and also to introduce a large volume of air into the apparatus.

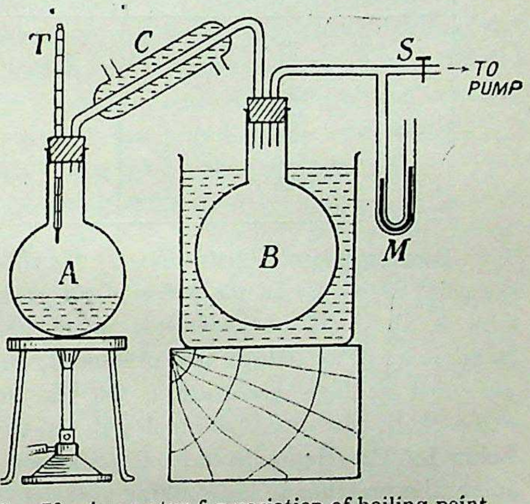


Fig. 78. Apparatus for variation of boiling point with pressure.

The pressure on the liquid is adjusted to any desired value by means of the pump and measured by the manometer M. When the required pressure has been arranged the stop-cock S is closed to cut off communication with the pump and the liquid is heated until it boils steadily and quietly ; a few bits of porcelain introduced in A promotes regular boiling. The temperature at which the liquid boils under a given pressure can thus be determined.

The results obtained completely verify that increase and decrease of pressure cause rise and fall respectively of the boiling point of the liquid. Data obtained in one of these experiments for water are given in the following table, which will indicate the magnitude of the effect.

External pressure in mm. of mercury	*Boiling point*
92	50°C
142	59°C
276	74°C
486	88°C
658	96°C
760	100°C
1075	110°C

Some *practical illustrations of the effect* of pressure on the boiling point are :—(*i*) In *the boiler of an express train,* when the pressure is about 15 atmospheres, water boils at about 200°C, unless steam is let off to reduce the pressure. (*ii*) *Pressure cookers* which are used at high elevations : On the top of high mountains, the atmospheric pressure is so much reduced that water boils at much below 100°C. Hence in order to cook food which requires 100°C and more, the pressure in the cooking vessel has to be increased by some contrivance, such as a pressure cooker, which is essentially a saucepan with a screw cover. (*iii*) *Sterilisation of surgical instruments.* Certain of these instruments have to be heated to a temperature much above 100°C in order to sterilise them, which is achieved by placing them in water boiling at high pressure. (*iv*) *Distillation at reduced pressure.* When a liquid, which decomposes at a temperature below its boiling point, has to be purified, it is distilled under reduced pressure, in order to prevent the decomposition.

4. Latent heat of vaporisation. The latent heat of vaporisation of a liquid is ordinarily defined as *the quantity of heat in calories required to change 1 gram of the liquid at its normal boiling point to vapour at the same temperature.* Thus the latent heat of vaporisation of water is the heat required to convert 1 gram of water at 100°C into steam at the same temperature. The *latent heat of condensation* is equal to the latent heat of vaporisation and is defined in a similar manner, but in the reverse order, since heat is evolved in the process.

The *latent heat of vaporisation is always much greater than that of fusion for the same substance.* Thus, for instance, the latent heat of vaporisation of water is about 540 calories whereas that of fusion of ice is only 80 calories. The reason for this great disparity can be readily understood. The internal work required to change a substance from liquid to vapour is considerably greater than to change it from solid to liquid, since in the former case the molecules should be pulled so far apart that they become quite independent of each other, whereas in the latter case the molecules are still bound by mutual attraction. Further, there is a much more marked increase of volume in vaporisation than in fusion, so that more external work also has to be done by change in volume in the former case than in the latter. It is therefore usual to distinguish two parts in the latent heat of vaporisation, *internal,* spent in internal work and *external,* utilised in external work. The latent heats of vaporisation of a few liquids are given in the following table :—

Liquid	*Normal boiling point*	*Latent heat of vaporisation (cals./gram)*
Mercury	357°C	68
Ether	34·6°C	83
Alcohol	78·3°C	206
Ammonia	—33·5°C	341
Water	100°C	538

The high latent heat of many vapours is made use of in the process of refrigeration, two of the commonest refrigerants being ammonia and sulphur dioxide.

Since the boiling point of a liquid can be varied widely by means of alteration of external pressure, it follows that *the latent heat of vaporisation cannot have a rigidly fixed value, but will vary with the external pressure and hence with temperature at which vaporisation takes place.* It will be shown presently that *it decreases as the temperature of boiling increases.* Strictly speaking, the latent heat of vaporisation at any temperature should be defined as the heat required to convert 1 gram of the liquid under an external pressure equal to that of the saturated vapour at that temperature into the saturated vapour at the same temperature.

Determination of the latent heat of vaporisation. In measuring the latent heat of vaporisation it is good to bear in mind that, since the quantity has a relatively high value and is involved in an isothermal change of state, the usual sources of error of the different methods of calorimetry will not vitiate results to any appreciable extent in the present case.

The various methods of determining the latent heat of vaporisation can be classified under three heads, *viz.*, *the method of mixtures*, the *constant flow method* and the *electrical method.* Under each class, slightly different and improved techniques have been used by different workers.

(*i*) **The method of mixtures**. The *basic principle* is to pass dry vapour of the liquid into a weighed quantity of water in a calorimeter of known temperature and note the rise of temperature of the calorimeter and contents. A final weighing of the calorimeter and contents readily gives the weight of the vapour condensed. If M be the mass of the water taken w the water equivalent of the calorimeter, θ_1 and θ_2 the initial and final temperatures of the calorimeter and contents, m the mass of the vapour condensed, θ the temperature of the vapour, and s the specific heat of the liquid, then we have

$$mL + ms(\theta - \theta_2) = (M + w)(\theta_2 - \theta_1)$$

from which L, the latent heat, can be found.

In the *simple laboratory experiment* of determining L of steam, the procedure is as follows : On account of the high value of L on the one hand, and since the maximum rise of temperature of calorimeter and contents should be kept within 30°C about to prevent evaporation on the other, the mass of steam condensed will be small compared to the mass of water used ; hence if steam is made to mix directly with the water, the mass of steam condensed cannot be accurately determined ; the steam is therefore passed into a separate *condenser* B fitted with an inlet and outlet for steam and kept completely immersed in the water of the calorimeter C (Fig. 79). Weighing the condenser separately, first empty before the experiment and then with condensed steam at the end, the mass of the condensed steam can be accurately determined.

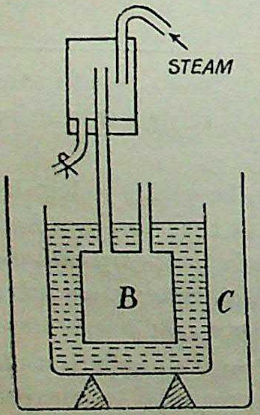


Fig. 79. Latent heat of steam.

In order to prevent condensed water, which is being carried along with the steam, from entering the condenser, the steam from the boiler is made to pass through a *trap* just before being let into the condenser, so that only dry steam enters the condenser, the condensed water being stopped in the trap and drained off through a side-tube.

All the time the steam is passed into the condenser, the temperature of the calorimeter and contents is above that of the surroundings and hence heat is lost by radiation. The correction for this loss is bound to be small, since the rise of temperature is fairly rapid, and can be eliminated by adjusting the initial temperature of the water to be as far below the room temperature as the final temperature is expected to be above it. If, however, greater accuracy is required, Barton's method of correction can be applied.

Finally, if the condenser is of a material different from that of the calorimeter, its water equivalent must be separately determined from its weight and specific heat.

Berthelot's apparatus. Berthelot, in his determination of the latent heat of steam, designed an elegant apparatus, in which not only the precautionary devices stated above but also a few others were incorporated. Supply of steam is obtained by boiling water in a glass vessel A provided with a central steam tube T, (Fig. 80), the heating being done with a ring burner B. Directly under the boiler the calorimeter C containing the condenser, which consists of a detachable spiral tube S and catch water D, communicating with the outside through a tube P is placed. The steam tube T is connected to the spiral of the condenser by a conical ground joint piece. The calorimeter with cold water completely covering the condenser is arranged in a constant temperature enclosure E and protected from the heat of the burner by an insulating cover F. The steam tube T

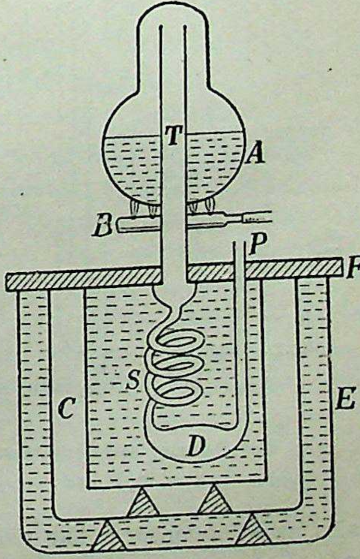


Fig. 80. Berthelot's latent heat apparatus.

is covered with asbestos at the section where it passes the burner to prevent the steam from being superheated.

In this design of apparatus, as the steam is made to pass through boiling water almost until it reaches the calorimeter, the amount of condensation occurring before the steam reaches the cold water is reduced to a minimum. The mass of steam condensed is determined accurately by weighing the condenser separately before and after the experiment. The pressure under which the boiling takes place is regulated by connecting the open end P of the condenser to a pump.

(*ii*) **Awbery and Griffiths' continuous flow method.** This method can be used not only for steam but also for the vapour of any liquid. Its chief feature is that the ordinary calorimeter is replaced by a continuous flow calorimeter. The liquid is boiled in a chamber which is electrically heated by an inner coil, so that the vapour supply can be had at a steady rate, essential for the experiment. An outer heating coil keeps the temperature of the surroundings almost the same as that of the vapour, thus eliminating cooling correction. The temperature of the vapour is measured by a thermocouple. The vapour passes down a long vertical tube surrounded by a water jacket through which water is circulated at a constant rate, so that the tube acts also as a condenser. The temperatures of the inflowing and outflowing water are measured by two thermocouples. Another thermocouple at the bottom end of the vertical tube measures the temperature of the condensed liquid leaving the apparatus (Fig. 81).

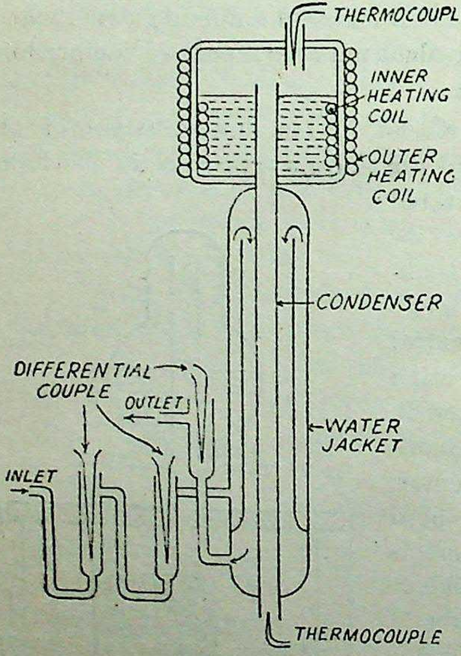


Fig. 81. Awbery and Griffiths' latent heat apparatus.

When the steady state is reached, the condensed liquid flowing out is collected for a known time and from its weight, the rate at which the vapour is condensed is obtained.

If M be the quantity of water flowing per unit time through the water jacket, θ the difference of temperature between the inflowing and outflowing water, m the mass of condensed liquid in unit time, θ_1 the temperature of the liquid as it leaves the apparatus, θ_2 the boiling point of the liquid and s the specific heat of the liquid, we have

$$\mathrm{M}\,\theta = m\,[\,\mathrm{L} + s\,(\theta_2 - \theta_1)\,]$$

from which L, the latent heat of vaporisation of the liquid, can be calculated.

(*iii*) **The electrical method.** The *principle* of this method consists in heating the liquid with an electric heater coil to its boiling point and allowing it to boil vigorously. If m is the loss in weight of the liquid due to vaporisation, E the p.d. between the ends of the heater coil in volts, I the value of the current in amperes and t the time of boiling, which is the same as that during which the current is passed,

$$m\mathrm{L} = \frac{\mathrm{EI}t}{\mathrm{J}}$$

from which L, the latent heat of vaporisation, can be calculated. A correction has to be made for the small vaporisation of the liquid which takes place independently of the electrical heating.

Different workers have employed this method for investigating the latent heat of vaporisation of different liquids under different conditions of temperature and pressure. Thus Ramsay and Marshall have used it for comparing the latent heats of various liquids. Henning has designed an apparatus on the same principle which is capable of giving results of great accuracy. As he has used it to measure the latent heat of vaporisation of water at different pressures, low and high, his technique will be described below where the variation of the latent heat with pressure and temperature is dealt with. Fogler and Rodebush have used the method to determine the latent heat of evaporation of mercury up to 200°C. Onnes and Dana and Simon and Lange have employed the method for measuring the latent heat of vaporisation of nitrogen, hydrogen, helium, etc., which liquefy at very low temperatures.

Variation of latent heat with temperature. As already mentioned, the latent heat of vaporisation varies with temperature, its value diminishing as the temperature at which boiling takes place is raised. Early investigators studied this point by measuring a quantity known as the **total heat**, usually represented by the symbol Q. The total heat of the saturated vapour of a liquid at any temperature t°C is defined as *the quantity of heat required to raise 1 gram of the liquid from 0°C to t°C and to convert it into the saturated vapour at t°C*. Previous to the classical experiment of Regnault on the total heat of steam, other workers had arrived at some strange results. Thus Watt had stated that the total heat of water vapour was independent of the pressure of the vapour and therefore of the boiling point of water. On the other hand, Creighton and Southern had held that the latent heat of water vapour was always a constant which meant that the total heat of steam varied with temperature, increasing as the boiling point of water was raised. Regnault, by his researches on the total heat of steam, was able to establish that both the above statements were incorrect.

Regnault's experiment. Regnault, using *the method of mixtures*, measured the total heat of steam at different external pressures and hence at different boiling points. Steam was produced by heating water in a boiler which was in communication with an air-chamber. By pumping air into or out of this chamber, the pressure on the water in the boiler could be varied and the water made to boil at any desired temperature, which was indicated by a thermometer inserted in the boiler; when high pressures were used, the bulb of the thermometer was protected against the influence of pressure by a suitable device. The condenser B immersed in water contained in a calorimeter C consisted of two communicating copper spheres and a copper spiral starting from the lower sphere and going out of the calorimeter. (Fig. 82). The free end of the spiral was connected to a manometer which measured the pressure of the steam used. The lower sphere was also provided with an outlet at its bottom to draw out the steam condensed during the experiment. The passage tube from

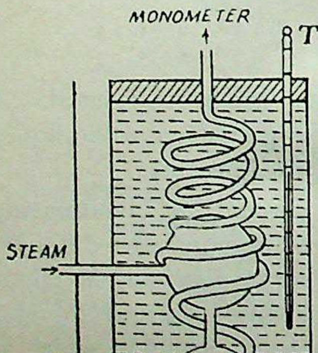


Fig. 82. Regnault's latent heat apparatus.

the boiler to the condenser was wrapped in non-conducting woollen stuff so as to prevent loss of heat. The steam formed in the boiler was passed downward through the boiling water by way of a spiral tube and then conveyed to the condenser. The steam entered the upper sphere of the condenser, passed into the lower one and then upwards through the spiral. The water condensed in the spiral and the spheres collected at the bottom of the lower sphere; it was drawn out into a beaker and weighed.

Noting the initial and final temperatures of the calorimeter and contents making the necessary correction for heat loss, the total heat of steam could be determined at any temperature corresponding to the pressure chosen. Regnault, varying the pressure from 0·2 to 13·6 atmospheres, determined the total heat of steam Q at different pressures and found that the value of Q at any temperature θ was given by the relation

$$Q = 606{\cdot}5 + 0{\cdot}305\theta \qquad \ldots (1)$$

By definition, the total heat Q is the sum of the heat required to raise 1 gram of water from 0°C to θ°C, *i.e.*, θ calories and of the heat required to convert 1 gram of water at θ°C to saturated vapour at the same temperature, *i.e.*, L_θ calories. Hence

$$Q = L_\theta + \theta$$

$$\therefore \quad L_\theta = Q - \theta = 606{\cdot}5 + 0{\cdot}305\theta - \theta$$

$$= 606{\cdot}5 - 0{\cdot}695\theta \qquad \ldots (2)$$

Relation (1) shows that the total heat Q increases with θ, thus disproving Watt's conclusion. Relation (2) indicates that L_θ decreases as the boiling point θ increases, which means that the statement of Creighton and Southern is also incorrect; it also establishes that the latent heat will vanish at a certain temperature, known as the *critical temperature* (θ_c). This temperature θ_c can be calculated from the relation

$$L_{\theta_c} = 606{\cdot}5 - 0{\cdot}695\theta_c = 0$$

Or $$\theta_c = \frac{606{\cdot}5}{0{\cdot}695} = 872°\text{C}$$

Experiment, however, gives for the critical temperature of steam a value of only 390°C. Hence, Regnault's empirical relation, giving indications in the right direction, cannot be taken as a general law.

Using the relation, in the case of boiling at normal pressure, *i.e.*, at 100°C, we get

$$L_{100} = 606{\cdot}5 - 0{\cdot}695 \times 100 = 537$$

which is very close to the accepted value; hence Regnault's expression is probably valid in the lower range of temperatures of boiling.

Henning's experiment. Henning using the *electrical method*, determined directly the latent heat of steam at different temperatures of boiling up to 180°C, corresponding to a pressure of about 10 atmospheres, with great accuracy. His experimental technique is rather complicated and we shall give here only its essential features, without entering into details. The water is heated electrically in air-tight bronze or copper vessel B which is fitted with two sealed tubes L and T, the former carrying the leads to the heater coil H and the latter a thermocouple thermometer for measuring the temperature of the steam. Loss of heat by radiation is eliminated by surrounding B with an electrically heated oil-bath whose temperature is maintained at that of the steam. The heater coil consists of constantan wire wound on a mica frame and enclosed in an air-tight box. Two pairs of leads go out from H, one to pass a current through the coil and the other to measure the p.d. between its ends. The steam produced in B passes down the tube T whose top end is bent down in order to prevent any drops of water entering it and goes to the condenser C, issuing as water from the lower end of it. For determining the latent heat at different temperatures, the pressure in the condenser is varied by connecting it to an air-chamber of large capacity which is maintained by means of a pump at any desired pressure indicated by an open manometer.

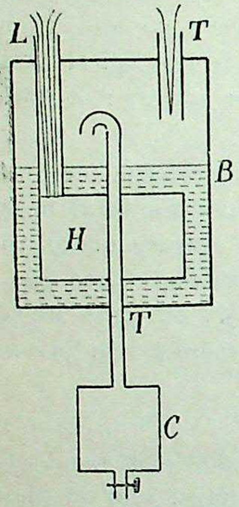


Fig. 83. Henning's latent heat apparatus.

When the rate of emission of the steam at a given pressure and hence at a given temperature of boiling is steady, the water leaving C in a known time is collected and weighed. The current passing through H and the p.d. across it are noted with an ammeter and voltmeter respectively in the external electric circuit. If m is the mass of water collected in t secs, E the p.d. in volts and I the current in amperes, then we have

$$mL = \frac{EIt}{J}$$

from which the latent heat of vaporisation L can be calculated.

Henning, as a result of his investigations, was able to show that the latent heat of vaporisation of water between 30° and 100°C was given by the formula

$$L = 538{\cdot}86 + 0{\cdot}5994\,(100 - t)$$

where $t = \theta_c - 1$

Similar empirical relations have been obtained by different workers, but none appears to be quite satisfactory. Experimental data of the latent heat of carbon dioxide at different temperatures plotted graphically clearly show its latent heat vanishes at its critical temperature, which is about 31°C.

The exact variation of the latent heat of vaporisation with temperature for all substances is given by a complicated thermodynamic formula :

$$\frac{dL}{dT} - \frac{L}{T} = C_g - C_l - \frac{L}{v_2 - v_1}\left\{\left(\frac{\partial v_2}{\partial T}\right)_p - \left(\frac{\partial v_1}{\partial T}\right)_p\right\}$$

where C_g and C_l are the specific heats of the substance in the gaseous and liquid states respectively and v_2 and v_1 the respective specific volumes.

5. Change of properties on vaporisation. (*a*) *Change of volume.* When a liquid changes into vapour, a great increase in volume takes place. For instance, 1 gram of water at 100°C occupies 1·043 c.c. When it is converted into 1 gram of steam at the same temperature, the latter occupies 1647 c.c. under normal pressure. From these data, the *internal and external latent heats of steam* can be estimated. The latent heat at 100°C = 539 cals./gm. External work done by change of volume is given by the product of the pressure and increase in volume, *i.e.*, by

$$(76 \times 13{\cdot}6 \times 980) \times 1647 = 1{\cdot}67 \times 10^9 \text{ ergs.}$$

$$\therefore \quad \text{External latent heat} = \frac{1{\cdot}67 \times 10^9}{4{\cdot}2 \times 10^7} = 39{\cdot}7 \text{ cals./gm.}$$

$$\text{Internal latent heat} = 539 - 39{\cdot}7$$
$$= 499{\cdot}3 \text{ cals./gm.}$$

(*b*) *Molecular latent heat of vaporisation—Trouton's rule.* As in the case of latent heat of fusion, here also we have Trouton's rule, which states that *the ratio of the molar latent heat of vaporisation to the boiling point is a constant.* If M is the molecular weight of the liquid, L its latent heat of vaporisation and T_b its boiling point in absolute scale, then

$$\frac{ML}{T_b} = \text{constant}$$

The value of the constant is found to be about 20 for most substances.

Since, however, the boiling point of a liquid varies greatly with external pressure, the boiling point T_b under normal atmospheric pressure is an artificial point, having no physical significance. On the other hand, the latent heat varies neither in the same direction nor to the same extent. Hence the ratio ML/T_b need not be a constant with a value of about 20 for all substances. In the case of water, it can be shown that the ratio goes on decreasing as the boiling point is raised, from a value of 40 at 0°C, 26 at 100°C, 16 at 230°C and finally zero at the critical temperature where the latent heat vanishes.

(c) *Spheroidal state.* An apparently singular phenomenon connected with vaporisation is what is known as the 'spheroidal state'. When a drop of water is let fall on a hot metal plate, the drop ordinarily spreads out and boils away with a hissing noise. If, however, the plate is very hot, the drop neither spreads nor boils but rolls about like a globule of mercury ; the drop is now said to be in a spheroidal state in which it is not really in contact with the hot plate, but is supported on a cushion of its own vapour. The temperature within the drop is found to be below its boiling point in such a state. The use of a hot metallic surface is not essential for the phenomenon ; the only necessary condition is a sufficiently high temperature which quickly forms a thick layer of vapour of the liquid to support the drop ; liquid drops may assume the spheroidal state on the surface of any liquid which is sufficiently hot. Researches show that the heat radiated by the hot surface to the drop is not sufficient to account for the phenomenon, but that the heat conducted through the vapour has a preponderant influence on the formation of the state.

Some interesting but puzzling facts can be explained on the basis of the spheroidal state. For example, the test of the laundry man to find whether his iron is hot by sprinkling water on it and seeing if spheroids form on it, the juggler's trick of licking red-hot iron, since contact of the tongue with the metal is prevented by the vapour developed, the freezing of water in a red-hot crucible containing liquid sulphurous acid, etc.

6. Properties of vapour. (*i*) **Vapour pressure**. The most important property of vapours, both from practical and theoretical points of view, is the pressure exerted by them. The pressure of steam and its variation with temperature, for instance, are essential for calculating the efficiency of different types of steam engines. Experimental data obtained from the study of vapour pressure have also been used to check the validity of theoretical laws of thermodynamics.

Although the term 'vapour pressure' is usually referred to the pressure exerted by saturated vapour, since it is a characteristic of the substance with a definite value at a definite temperature, it must be borne in mind that unsaturated vapour also exerts pressure, as already indicated ; it will be presently seen that the two types of vapour pressures, saturated and unsaturated, obey different laws.

The pressure exerted by vapours varies over a very wide range, from as low as 10^{-6} mm. to as high as 400 atmosphere. Hence experimental determination of vapour pressure will naturally require different kinds of apparatus. Regnault proved himself not only a pioneer but also an efficient worker in this matter, as in other problems of heat.

MEASUREMENT OF VAPOUR PRESSURE

The methods used for measuring saturated vapour pressure can be classified under two general heads :—

Static or *direct methods*, in which the temperature is fixed and the pressure is determined manometrically.

Dynamic or *boiling point methods*, in which the pressure is fixed and the temperature at which the liquid boils is determined.

The former is suited for low temperatures while the latter for high.

Statical method. Dalton was the first to determine the saturated vapour pressure of water with accuracy by this method. But Regnault, using an apparatus, similar to that of Dalton but improved, made more detailed researches on the saturated vapour pressure of water in the range 0°C to 50°C.

Regnault's apparatus. Two barometer tubes are set up side by side, fed from the same cistern of mercury. The upper ends of the two tubes are enclosed in a water-bath B provided with a plane glass front. The bath can be heated by passing steam into it and maintained constant at any desired temperature by stirring the water well and noting the temperature with a thermometer T. Water is introduced into one of the barometer tubes with a bent pipette until the space above the mercury is saturated, which will be the case when a layer of water remains floating on the mercury surface. Due to the pressure exerted by the saturated vapour of water at the given temperature of the bath, the mercury level will go down.

The difference in levels of the mercury surfaces in the two tubes, read by a cathetometer through the *plane* glass window which eliminates error due to refraction, gives the saturated vapour pressure of water at the temperature of the bath. Maintaining the bath at different constant temperatures and repeating the experiment, taking care that there is always a layer of water in the experimental tube, the saturated vapour pressure at different temperatures can be found. Corrections have to be made for :—(*a*) *the pressure due to the water layer in the experimental tube* ; it is given by $h\rho/\rho'$, where h is the height of the layer, ρ the density of water and ρ' that of mercury, and is *substracted* from the observed difference in levels of mercury ; (*b*) *the effect of surface tension*, which introduces a small difference in levels of mercury in the two tubes, independently of the vapour pressure ; in the case of water, the height of mercury in the experimental tube will be slightly higher than in the reference tube, so that the correction has to be *added* to the difference in level due to the vapour pressure ; (*c*) *the reduction to the corresponding height of mercury at 0°C*, as the vapour pressure is ordinarily expressed in terms of the height of mercury at 0°C.

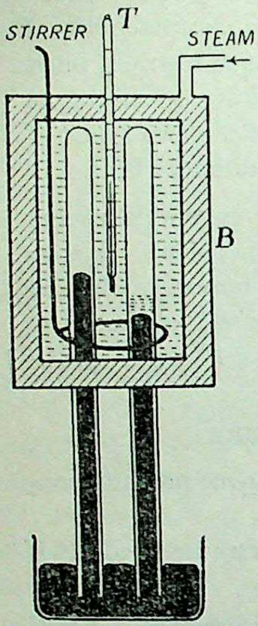


Fig. 84. Regnault's vapour pressure apparatus.

It is to be noted that, since as the temperature is raised the vapour pressure increases, when it becomes greater than about 10 cms., corresponding to a temperature of about 50°C, the apparatus is no longer suitable as the water bath would have to be enlarged to such an extent that it would be impossible to maintain its temperature uniform.

For temperatures below 0°C, Regnault modified his apparatus as follows. The top of the experimental tube is bent round and terminates in a spherical bulb which contains water or ice and is surrounded by a suitable low-temperature bath. Later workers have employed a better type of apparatus, though working on the same principle, which can be used for finding the vapour pressure of any liquid at low temperatures, provided the liquid does not react on mercury and the vapour pressure is not too low. We shall now describe one such apparatus.

Apparatus for measuring vapour pressure of any liquid at low temperatures. It consists of a bulb provided with suitable connections to the supply of the vapour under test, a pump and a mercury manometer, the different sections being manipulated by taps, as shown in Fig. 85.

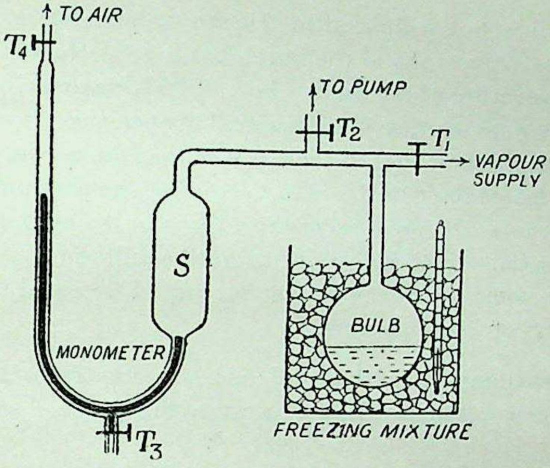


Fig. 85. Apparatus for vapour pressure at low temperature.

The apparatus is first evacuated by keeping T_1 closed and T_2 open. The bulb is then placed in a bath containing suitable freezing mixture and the tap T_2 is closed and T_1 is opened, which lets in the vapour into the bulb, which begins to condense as soon as the apparatus is saturated. When sufficient liquid has been thus formed in the bulb, the tap T_1 is closed and the difference of levels in the manometer is noted using a cathetometer. The tap T_3 is then opened and mercury is pumped into the manometer until the space S is full. The difference of levels is again noted and should be the same as before. If the left-hand side of the manometer has been previously exhausted with the help of a pump and tap T_4, the above noted difference of levels, corrected to 0°C, gives the vapour pressure of the liquid at the temperature of the bulb, indicated by a thermometer inserted in the freezing mixture maintained at any desired constant temperature. If, on the other hand, the manometer is open to the atmosphere, the noted difference of levels must be added to or subtracted from the barometric height, according as the left-hand side level is the higher or lower.

It is to be noted that, although the manometer is at a higher temperature than that of the bulb, it still gives the vapour pressure at the temperature of the bulb. For, if the vapour in the manometer part were saturated at its actual temperature, it would be at a higher pressure than that in the bulb, so that the vapour would flow from the manometer to the bulb to equalise the pressures. But any attempt to raise the pressure of the vapour in the bulb simply results in condensation which will continue until equilibrium is established when the pressure of the vapour is everywhere equal to that at the coldest part of the apparatus.

Maintaining the bath at different low temperatures, the variation of vapour pressure with temperature in the range studied can be found.

This type of apparatus is well suited fer measuring vapour pressures of different liquids, ranging from a few cms. to the atmospheric pressure ; it can be used to measure the vapour of ice and has been applied in the case of permanent gases between their freezing and boiling points. Thus Henning and Stock have employed this method for measuring the vapour pressure of a number of gases between + 10 and − 181°C. On the same principle, *vapour pressure thermometry at low temperature* has been developed as we shall see later.

It may also be noted that Holborn and Baumann have determined the vapour pressure of water above 290°C by the statical method.

Apparatus used in the laboratory. Joly's apparatus, which has been described in connection with the measurement of the pressure coefficient of air (*Cf.* p. 97). is used as a statical method for the laboratory experiment of determining the saturated vapour pressure of water at different temperatures in the ordinary range, say between the room temperature and the boiling point of water ; it is based on Dalton's law of pressures (*Cf.* below) and involves the knowledge of the value of the vapour pressure at some particular temperature, say the room temperature, which can be readily obtained from tables.

Some water is introduced in the bulb of the apparatus, so that a small quantity of it always remains and the bulb is thus always filled with a mixture of air and saturated water vapour. The bulb is kept immersed in a beaker of cold water whose temperature t_1 is noted with a thermometer. The movable limb is adjusted until the level of mercury in the other coincides with the fixed mark, thus keeping the volume constant. The readings of the levels of mercury in the two limbs are taken and the difference of levels h_1 is obtained. The pressure of the mixture of air and vapour in the bulb is given by $(H \pm h_1)$ where H is the barometric height corresponding to the atmospheric pressure. The vapour pressure h of water at the temperature of cold water (t_1) being assumed from tables, the pressure of the air alone is $H \pm h_1 - h$.

The water in the beaker is heated and its temperature is maintained constant at any desired value t_2. The apparatus is quickly adjusted to have the mercury level coincide with the fixed mark and the new difference in levels h_2 in the two limbs is found. The total pressure of the mixture of air and vapour at t_2°C is $H \pm h_2$.

If p_0 is the pressure of air at 0°C and α its pressure coefficient, then

$$H \pm h_1 - h = p_0 (1 + \alpha t_1)$$

Similarly, $$H \pm h_2 - x = p_0 (1 + \alpha t_2)$$

where x is the pressure of the vapour at t_2°C.

$$\therefore \quad \frac{H \pm h_1 - h}{H \pm h_2 - x} = \frac{1 + \alpha t_1}{1 + \alpha t_2}$$

Assuming the value of $\alpha = 0{\cdot}0037$, the above equation is solved for x, which is the only unknown in it. Thus the vapour pressure at a given temperature is found.

By keeping the bulb at different steady temperatures, the vapour pressure at these temperatures can be determined.

The same results may also be obtained by a *graphical method* as follows. Plotting the total pressure of the mixture as ordinates against the temperature as abscissae, the curve AB is obtained (Fig. 86). If AC represents the known saturated vapour pressure at the temperature t_1, CE represents the pressure of air alone in the bulb at the same temperature. The pressure coefficient of air α

being known, DF representing the pressure of air alone at another temperature t_2 can be calculated from the relation

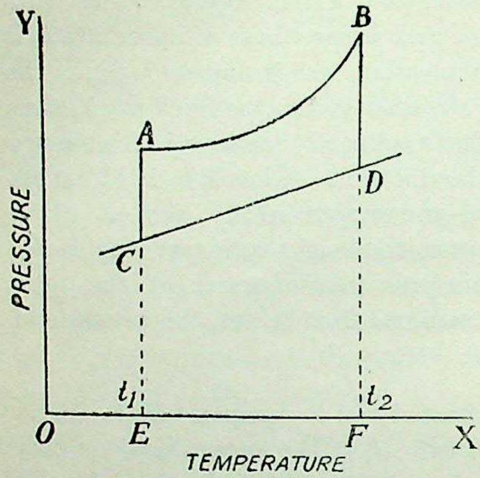


Fig. 86.

$$\frac{\mathrm{CE}}{\mathrm{DF}} = \frac{1 + \alpha t_1}{1 + \alpha t_2}$$

Thus the point D is obtained. The line joining C and D is the graph connecting the pressure and temperature of air alone and hence must be a straight line. The intercepts between the curve AB and the straight line CD give the saturated vapour pressure at the intermediate temperatures in the range t_1 to t_2.

Dynamical method. This method is well suited for high temperatures, while most of the statical apparatus described above are useful up to about 100°C. It is based on the principle that the saturated vapour pressure of a liquid at its boiling point is equal to the external pressure to which it is subjected. Hence it is known also as the *boiling point method*. It is called *dynamical*, because the liquid continually boils away, in contrast to the *statical method* where the liquid remains stationary.

Regnault's apparatus. Regnault designed an apparatus based on this dynamical principle, for measuring the saturated vapour pressure of water between 50°C and 200°C. It is shown in Fig. 87.

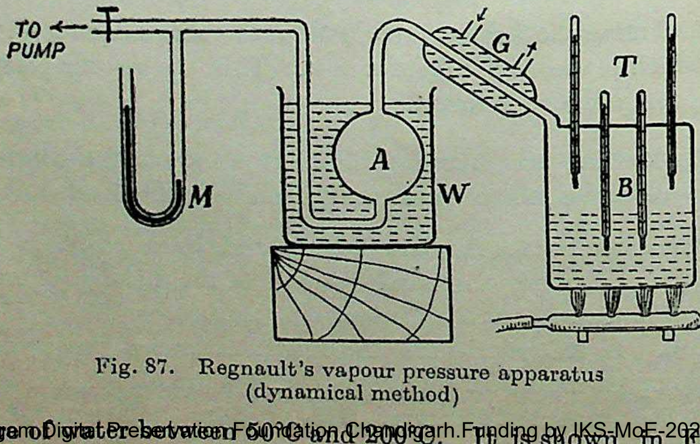


Fig. 87. Regnault's vapour pressure apparatus (dynamical method)

A copper boiler B which contains the experimental liquid (water), is connected through a condenser G to a large copper air chamber A kept immersed in constant temperature water bath W. Connecting this chamber to a pump, the pressure in the boiler can be maintained at any desired value, indicated by a mercury manometer M. The large capacity of A as well as its constant temperature serve to smoothen out any fluctuations due to the movement of mercury in the manometer or due to the initial issue of vapour, thereby enabling the pressure to be changed by small amounts. The boiler is heated and the liquid in it begins to boil as soon as its vapour pressure is equal to the external pressure. Quiet and regular boiling is secured by putting a few porcelain bits in the boiler. The vapour produced is condensed in G and the liquid flows back into the boiler, with the result that the liquid is not wasted and the pressure is prevented from rising. The boiling point is determined from the mean of the readings of four thermometers T inserted in the boiler, two immersed in the liquid, two in the vapour above. The pressure corresponding to this boiling point, as indicated by the manometer, gives the saturated vapour pressure at the temperature of boiling.

Increasing the pressure step by step, until the maximum pressure which the apparatus can stand is reached, the boiling point is measured for each value of the pressure. Thus Regnault altering the pressure up to 28 atmospheres, was able to investigate the vapour pressure of water from 50°C to about 200°C.

The method is capable of great accuracy and can be used also for liquids other than water. It can be adapted for very high pressures provided all the parts are made of copper and a force pump is used. With suitable modifications, even very small vapour pressures can be measured by this method, as Ramsay and Young did. Braun applied this method to metals like zinc and cadmium. The metal is heated electrically in a porcelain crucible and the temperature of the vapour is measured by a thermocouple.

Results. The results obtained from investigations on the vapour pressure of liquids may be summarised as follows :—

(*a*) *Effect of temperature on vapour pressure.* Experiments establish beyond doubt that *the saturated vapour pressure of every substance increases with rise of temperature.* In the following table, the values obtained in the case of water are given.

Temperature	*Saturated vapour pressure*	*Temperature*	*Saturated vapour pressure*
−10°C	2·1 mm.	60°C	149·2 mm.
−5 ,,	3·1 ,,	70 ,,	233·5 ,,
0 ,,	·6 ,,	80 ,,	355·1 ,,
5 ,,	6·5 ,,	90 ,,	525·8 ,,
10 ,,	9·2 ,,	100 ,,	760·0 ,,
20 ,,	17·5 ,,	110 ,,	1074·5 ,,
30 ,,	31·7 ,,	120 ,,	1489·0 ,,
40 ,,	55·1 ,,	150 ,,	3569·0 ,,
50 ,,	92·3 ,,	200 ,,	11647·0 ,, (15·4 atmos.)

If these data are plotted, a curve of the form shown in Fig. 88 is obtained. From the graph it is seen that *not only the saturated vapuor pressure increases with temperature but also its rate of increase becomes greater, the higher the temperature.*

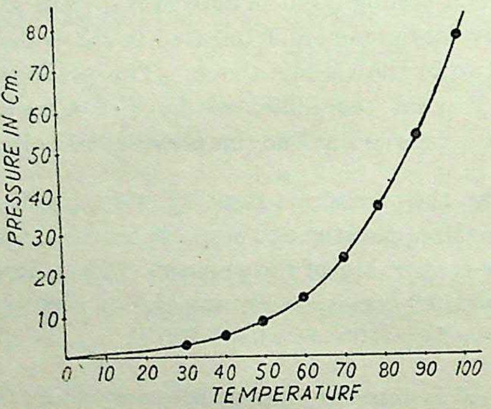


Fig. 88. Variation of vapour pressure of water with temperature

But it has not been possible to express the relation between the saturated vapour pressure and temperature by a simple correct formula. A number of empirical relations have been proposed, which, however, agree with experimental results only for limited ranges, none of them being quite exact and universal. Thus, for instance, Young proposed the formula

$$\log p = \mathrm{A} + \frac{\mathrm{B}}{\mathrm{T}} \qquad \ldots(1)$$

where p is the saturated vapour pressure at the absolute temperature T, and A and B are constants.

Kirchhoff and Rankine suggested quite independently a relation of the form

$$\log p = A + \frac{B}{T} + C \log T$$

This equation seems to represent pretty closely experimental data ; it has the additional merit that it can be deduced from theoretical considerations.

If *the temperature is lowered*, some of the vapour condenses, so that the vapour still remains saturated but exerts a lower pressure corresponding to the lower temperature.

Thus, for any given vapour, there is for each temperature a definite saturation pressure corresponding to that temperature. Hence also *the saturated vapour pressure is not effected by change of volume, i.e., does not obey Boyle's law.* If the volume occupied by the vapour is increased, more liquid evaporates, so that its saturation pressure remains constant ; if the volume is decreased some of the vapour condenses so that the saturation pressure of the vapour again remains the same.

Unsaturated vapours, on the other hand, behave approximately like gases ; they obey the laws of Boyle and Charles, but deviate from them more and more as the pressure increases towards the saturation value. Thus if the temperature of an unsaturated vapour at constant pressure is raised or lowered, it expands or diminishes in volume according to Charles' law ; in the latter case the volume decreases until a temperature is reached for which its pressure is equal to the maximum vapour pressure, and the vapour becomes saturated, any further cooling producing condensation of some vapour. At a given temperature, if the volume occupied by an unsaturated vapour is altered, its pressure will change according to Boyle's law. If the volume is increased, the pressure will decrease ; if the volume is decreased the pressure will increase until it reaches a value which is equal to the maximum vapour pressure for the given temperature and the vapour becomes saturated, any further change producing condensation.

These considerations throw further light on the *distinction between a vapour and a gas.* An unsaturated vapour at temperatures considerably higher than the boiling point of the liquid from which it is formed may be treated as a gas. Experiments described in a later chapter will show that there is a temperature called the *critical temperature*, below which a substance in the gaseous state can be liquefied by increasing the pressure until the saturation pressure for the temperature is reached. The term 'vapour' is applied to such a substance, which is really unsaturated vapour. If, on the other hand, the substance in the gaseous state is above the critical temperature it cannot be liquefied by increase of pressure, however great, and is called a 'gas'.

(*b*) *Pressure of a mixture of vapours.—Dalton's law of partial pressures.* When a mixture of vapours (or gases) which do not chemically interact with each other are present in the same enclosure, the pressure exerted by each constituent is the same as that which it would exert if it alone occupied the whole volume. The total pressure of the mixture is therefore equal to the sum of the pressures exerted by the constituent vapours, which are called *partial pressures*. This law applies both for saturated and unsaturated vapours, but with the difference that when the volume of the enclosure is altered, the pressure of the former remains constant while that of the latter changes according to Boyle's law.

The same law is found to hold good for the vapour pressure of a mixture of liquids provided they are insoluble in each other. If, however, the liquids are soluble in each other, the vapour pressure of the mixture is found less than the sum of the vapour pressures of the constituent liquids.

(*ii*) **Vapour pressure over curved surfaces.** The pressure of a saturated vapour in equilibrium with its liquid is not the same when the liquid surface is curved as when it is plane, due to surface tension. This can be explained in a simple manner as follows :—

A molecule will escape from the surface of the liquid if its kinetic energy is sufficient to carry it beyond the range of attraction of other molecules in the liquid surface. The force of attraction pulling down the escaping molecule is larger, the greatar the number of molecules of the liquid which lie within the range of attraction. Now since the number of these attracting molecules varies according to the shape of the surface, being greater if the surface is concave, less if convex, than that in the case of a plane surface, as

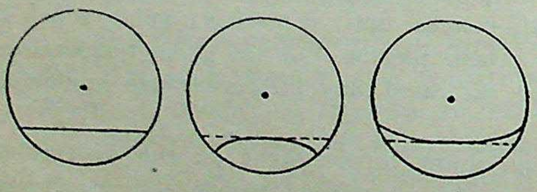


Fig. 8 .

seen from Fig. 89, the force of attraction also will correspondingly vary accordingly to the shape of the surface. Hence at a given temperature *the rate of escape of molecules from a liquid with a convex surface is greater, with a concave surface less, than in the case of a plane surface.* Now, since the saturated vapour pressure of a liquid is proportional to the rate of escape, *above a convex surface the vapour pressure must be greater, and above a concave surface it must be less than that above a plane surface.*

An expression for the vapour pressure over a curved liquid surface can be obtained as follows :—

When a capillary tube is inserted vertically into a liquid, in many cases the liquid in the capillary tube stands at a higher level A than the general level B, and its surface is curved concave upwards, as shown in Fig. 90. Let such an arrangement be placed in an evacuated vessel, so that the whole space above the liquid is filled with a vapour of the liquid.

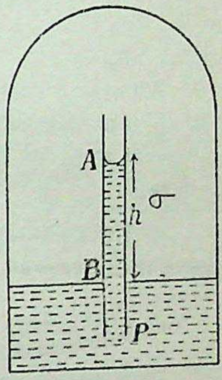


Fig. 90. Effect of curvature on vapour pressure.

There is a state of equilibrium between the liquid and its vapour both at A and B ; otherwise evaporation or condensation will occur until equilibrium is reached. The pressure at B exceeds that at A due to a column of the vapour of height AB. It follows that the vapour is in equilibrium with the liquid at a lower pressure at A where the surface of the liquid is concave than at B where the surface is plane.

If p and p' are the vapour pressures at B and at A respectively, h the height of AB, and σ the density of the vapour (assumed constant),

$$p - p' = hg\sigma \qquad \dots (1)$$

If T is the surface tension of the liquid and r the radius of curvature of the concave surface at A, the pressure just under that curved surface is given by $p' - \frac{2T}{r}$. If the liquid pressure at B is P, and ρ the density of the liquid

$$P = p' - \frac{2T}{r} + hg\rho \qquad \dots (2)$$

Now for equilibrium between the liquid and its vapour at B $P = p$. Hence

$$p = p' - \frac{2T}{r} + hg\rho$$

Or $$p - p' = hg\rho - \frac{2T}{r}$$

Comparing this with (1)

$$hg\sigma = hg\rho - \frac{2T}{r}$$

Or $$h = \frac{2T}{r} \cdot \frac{1}{g\,(\rho - \sigma)}$$

Substituting this value of h in (1)

$$p - p' = \frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma} \qquad \ldots (3)$$

Representing the difference in vapour pressure over a plane and curved surface by $\triangle p$

$$\triangle p = \frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma} \qquad \ldots (4)$$

Above a concave surface the vapour pressure must be less by this amount $\triangle p$ than that over a plane surface, while above a convex surface it must be greater by the same $\triangle p$ than that over a plane surface.

If the variation of vapour density σ with the height h is also taken into account, relation (4) becomes

$$\log_e \frac{p}{p'} = \frac{2T}{r} \cdot \frac{\sigma}{p\rho} \qquad \ldots (5)$$

Consideration of relation (4) leads to important conclusions concerning *the phenomenon of boiling and the formation of clouds.* If r is large, $\triangle p$ becomes small ; if r is very small, $\triangle p$ becomes very large.

Hence in the *process of boiling* if there are nuclei of sufficiently large radii due to the presence of dust particles or of porcelain bits placed in the liquid, the bubbles formed round these nuclei are fairly big, so that the excess pressure due to surface tension is of moderate amount and the vapour pressure can easily support it along with the hydrostatic pressure, thereby leading to the normal and regular boiling. If on the other hand, there are no or only very small nuclei present, the excess of pressure due to surface tension will be extremely large, so that the vapour pressure at the formation of the bubbles cannot support it and this will lead to superheating where the equilibrium between vapour pressure and hydrostatic pressure will be very unstable with the consequent boiling by bumping.

The *formation of clouds*, mists and fogs can be explained in a similar manner. Clouds, mists and fogs are aggregates of minute water drops, which, in general, are formed round dust particles. These act as nuclei of appreciable radii of curvature, so that the supersaturation pressure $\triangle p$, due to cooling of the atmosphere laden with water vapour does not have to be so large as under dust-free conditions. Hence presence of nuclei in the atmosphere due to dust particles or electric charges favour the formation of clouds, mists and fogs with comparative ease. If such nuclei were absent, no clouds will be formed even if the atmosphere is saturated with water vapour and cooled to a temperature below the dew-point.

(*iii*) **Vapour density.** This quantity is strictly defined as the mass of unit volume of a vapour at a given temperature and pressure. But in practice, it is often defined as *the mass of given volume of a vapour divided by the mass of an equal volume of air or hydrogen at the same temperature and pressure.*

Let w be the weight of a volume v of a vapour at a pressure p and temperature T (absolute). Let w_0 be the weight of air per unit volume at 0°C and 76 cm. pressure. Then the weight w' of a volume v of air at a pressure p and temperature T is given by

$$w' = w_0 v \times \frac{p}{76} \times \frac{273}{T}$$

$$\therefore \quad \text{Vapour density } \rho = \frac{w}{w'} = \frac{w}{w_0 v} \times \frac{T}{273} \times \frac{76}{p} \quad \ldots (1)$$

Since $w_0 = 0{\cdot}001293$ gm./c.c., ρ is determined if the volume, temperature and pressure of a known weight w of the vapour are known.

If the vapour obeys the gas laws to the same extent as air, then, since $pv = RT$

$$\rho = \frac{w}{w_0} \cdot \frac{76}{273\ R} \quad \ldots (2)$$

This relation (2) shows that the vapour density thus determined is independent of pressure and temperature. But experimental investigations carried out with great care, as was done by Regnault, indicate that ρ increases as the vapour approaches the saturation stage. This is due to the fact that the vapour fails to follow Boyle's law at pressure exceeding 0·8 of the saturation pressure. No perfectly general and accurate law connecting the pressure, volume and temperature of a vapour right up to its condensation point has yet been discovered.

The use of hydrogen as the standard substance instead of air in the determination of vapour density has been more fruitful from the chemist's point of view, since the measurement of vapour density offers a simple means of finding the molecular weight of a substance. According to Avogadro's hypothesis, equal volumes of all gases at the same temperature and pressure contain equal number of molecules. Hence the vapour density of a substance with hydrogen as the standard is equal to the ratio of the mass of a molecule of the substance to that of a molecule of hydrogen. Since the molecular weight of hydrogen is 2, the *vapour density of a substance is half its molecular weight.* For this purpose the vapour density need not be determined very accurately. All that is required is an approximate value of the molecular weight to fix up the valency. The precise value can then be calculated easily.

It is usual to determine the *density of the permanent gases,* like air, hydrogen, etc., according to the strict definition, *viz.*, as the ratio of the mass to the volume at 0°C and 76 cm. pressure. The principle of the method is as follows. A bulb is surrounded with melting ice (0°C) and filled with the gas at atmospheric pressure P. It is then closed and weighed. Next reducing the pressure of the gas to another value p, the bulb is closed and weighed again. If v is the volume of the bulb at 0°C, the mass of the gas in it at the end of the experiment occupies a volume v at 0°C and a pressure p; the same mass of gas would occupy a volume $\frac{pv}{\mathrm{P}}$ at 0°C and a pressure P. If w is the difference between the two weighings of the bulb, then w is the mass of $\left(v - \frac{pv}{\mathrm{P}}\right) = \frac{v(\mathrm{P} - p)}{\mathrm{P}}$ of the gas at 0°C and a pressure P or of $v\,\frac{(\mathrm{P} - p)}{76}$ at 0°C and 76 cm. pressure. The density of the gas is therefore given by

$$\frac{\text{mass}}{\text{volume}} = \frac{w}{\dfrac{v(\mathrm{P} - p)}{76}}$$

Determination of vapour density. Up to the time of the classical experiment of Fairbairn and Tate in 1860, no method was devised for directly determining the density of saturated vapours. All the previous methods of Victor Meyer, Gay Lussac, Dumas, Hofmann and others were indirect : the density of the unsaturated vapour was experimentally determined and assuming the gas laws to hold right up to the saturation stage, the density of the saturated vapour was deduced. Since, this assumption cannot be fully justified, this method of procedure cannot give an accurate value of the density of the saturated vapour. Still the methods of measuring the density of unsaturated vapour are of practical importance, chiefly that of Victor Meyer, as they provide an easy means of determining the molecular weight. We shall therefore first describe Victor Meyer's method and then pass on to the direct determination of the density of saturated vapour.

Victor Meyer's method. The apparatus (shown in Fig. 91) consists of a vertical glass tube G provided with a cylindrical bulb at its lower end and a side-tube S near its top, which dips in a pneumatic trough under a graduated jar J filled with water and kept inverted for collecting the air displaced by the vapour. A rubber cork C closes the upper end of the tube. At the bottom of the bulb a little mercury is placed in order to avoid breakage when the bottle containing the liquid which is to be vapourised is dropped. The bulb and a good part of the stem of G are enclosed in a hot-bath H containing water or some other suitable liquid whose boiling point is well above that of the experimental liquid. When the bath is steadily heated, the air inside G is expelled until a steady state is reached when no more air escapes. The side tube S is inserted into the inverted jar J only after this steady state is obtained, which is indicated when no more air-bubbles come out of the side-tube.

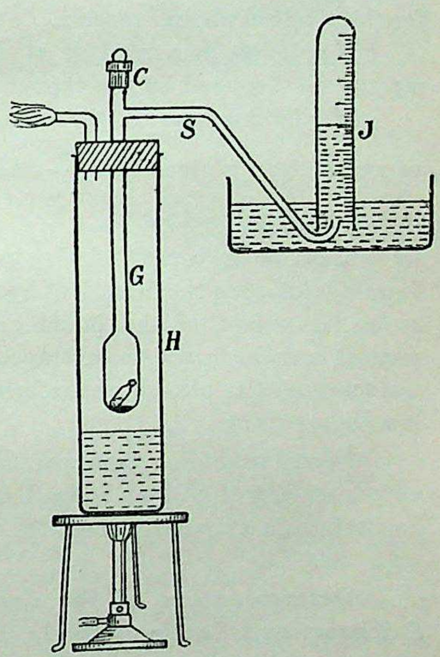


Fig. 91. Victor Meyer's apparatus.

A known mass of the liquid, whose vapour density is to be determined, is put inside a small stoppered bottle. The bottle is dropped into the tube G and the cork C is quickly and tightly closed. The liquid vaporises and forces off the stopper. The vapour thus formed displaces an equal volume of air which passes through the side tube into the inverted jar. This volume is readily measured since the jar is graduated, taking care that the level of water inside and outside the jar is the same. The temperature t of the water in the trough and the atmospheric pressure P are noted. If v be the volume of air thus measured at the actual temperature and pressure of the experiment, the volume v_0 at N.T.P. is given by

$$v_0 = v \cdot \frac{P - h}{76} \cdot \frac{273}{273 + t}$$

where h is the aqueous vapour tension at the temperature t (readily obtained from tables). The atmospheric pressure has to be corrected for this aqueous vapour tension.

If ρ_0 be the density of air at N.T.P. (taken from tables) the mass of air displaced by the vapour $= v_0\rho_0$.

If w be the mass of the liquid used in the experiment, the vapour density is given by $\frac{w}{v_0\rho_0}$, *i.e.*, the mass of liquid divided by that of the displaced air.

The vapour density relative to that of hydrogen can also be found by knowing the density of hydrogen at N.T.P., and hence the molecular weight of the liquid can be readily evaluated. This method is well adapted to substances which are liquid at ordinary temperatures like alcohol, chloroform, etc., and have a comparatively low boiling point.

Nernst modifying the apparatus has been able to determine the vapour density of KCl and NaCl up to 2000°C. Wartenburg has determined in a similar manner the vapour density of several metals up to 2000°C.

Determination of the density of saturated vapours—Fairbairn and Tate's method. It is of importance to devise a method of directly and accurately determining the density of a saturated vapour in order to find the nature and extent of the deviation from Boyle's law at the saturation stage. Fairbairn and Tate were the first to achieve this. From Andrews' researches on carbon dioxide it could be established that *the pressure of saturated vapour increases more rapidly with temperature than the pressure of unsaturated vapour*. This fact was utilised by Fairbairn and Tate in devising their apparatus, the principle of which is illustrated in Fig. 92. A and B are two bulbs containing water, with a larger quantity in B than in A, separated by a column of mercury.

All air is expelled from the arrangement, so that the space above the liquid in both the bulbs contains only saturated vapour. The apparatus is completely immersed in a water-bath whose temperature is steadily increased. The levels of mercury in the two limbs remain constant, that in A being slightly higher than in B on account of the greater amount of water in B. But as soon as the temperature reaches a value at which all the liquid in A disappears, and the vapour in it begins to become unsaturated, the level of mercury in A suddenly rises, since the pressure of saturated vapour rises much faster with temperature than that of the unsaturated vapour. In the same manner, the big difference of levels will suddenly drop at the temperature at which the vapour in A becomes saturated when the bath is being cooled down again. Hence the temperature at which the bulb A becomes filled with saturated vapour can be obtained as a mean of the two observations mentioned above, *viz.*, sudden increase and drop in the difference of levels. Knowing the mass of the water which was originally introduced in A and the volume of the space in A above the level of mercury, the density of the saturated vapour at the temperature noted and the corresponding pressure can be calculated.

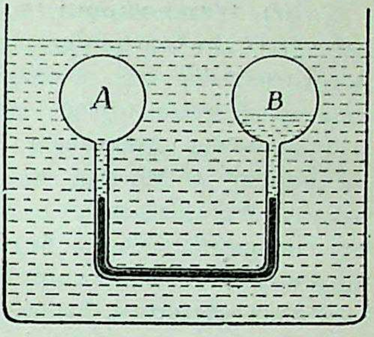


Fig. 92.
Fairbairn and Tate's apparatus.

Fairbairn and Tate found that the density of saturated steam was decidedly greater than that calculated from Boyle's law. Their results have been confirmed in the case of other vapours also by other workers. One may therefore safely conclude that vapours do not obey Boyle's law up to the point of saturation ; they become more compressible than the law allows as the point of condensation is approached.

Fairbairn and Tate found that the volume of 1 gram of saturated steam at 100°C and 76 cm. pressure is 1641 c.c. But later and more accurate measurements give the value 1677 c.c. which is much closer to the theoretical value obtained from the thermodynamical latent heat equation, as we shall see later. The lower value obtained by Fairbairn and Tate is probably due to the occlusion of steam by the walls of the bulb.

It may be noted that the density of saturated vapours can also be determined by isolating a portion of the saturated vapour and weighing it, as Perot has done.

(*iv*) **Water vapour in the atmosphere—Hygrometry.** On account of the constant evaporation from the surface of water in the sea, rivers, lakes, etc., atmospheric air always contains a certain amount of water vapour. We have seen that there is a maximum pressure for the water vapour in space for every temperature, which is independent of whether the space contains air or not. Hence the capacity of the atmosphere to hold water vapour is limited and depends upon temperature alone. At any given temperature, the atmospheric air can normally contain only that much of water vapour which exerts maximum pressure at that temperature : in such a case the atmosphere is said to be saturated ; if it contains less than that maximum amount, it is unsaturated ; in some cases the atmosphere may contain more than the maximum amount, when it is said to be supersaturated. The actual amount of water contained in the atmosphere, usually expressed in terms of its density or the pressure it exerts, is known as the *absolute humidity* of the atmosphere.

Relative humidity. It is to be noticed that it is not the absolute pressure of water vapour present in the atmosphere which determines its humidity, but its relation to the saturation vapour pressure at the actual temperature of the atmosphere. For, a given vapour pressure may be sufficient to saturate the air on a cold wet day, whereas the same pressure is unable to do so on a hot dry day. Hence the humidity of the atmosphere is usually estimated by the *relative humidity*, which is defined as *the ratio of the mass of water vapour actually present in unit volume of the atmospheric air to the mass of water vapour necessary to saturate the same volume at the temperature of the atmosphere.*

Since at any given temperature the mass of water vapour present in a given volume of air is very nearly proportional to the pressure exerted by it, relative humidity may be defined also as *the ratio of the pressure exerted by the water vapour actually present in the atmosphere to the saturation vapour pressure at the temperature of the atmosphere.*

As the relative humidity is a ratio it is a mere number and is conveniently *expressed as a percentage*. The relative humidity of the atmosphere is also called the *hygrometric state* of the atmosphere (from the Greek word *hugros*=wet or moist.)

Dew-point. If air containing moisture is progressively cooled, a stage is reached when the moisture it contains is sufficient to saturate it. Any further cooling will make the water vapour condense on the surface of the containing vessel in the form of "dew". The temperature at which this phenomenon occurs is called the *dew-point*, *i.e.*, the temperature at which the vapour present would saturate the air. In the case of the atmosphere, the dew-point is defined as *the temperature to which the atmosphere should fall in order that the water vapour actually present in it would saturate it.* From this it follows that the pressure of unsaturated vapour in a place is numerically equal to the pressure of saturated vapour at the dew-point for the place. Hence the relative humidity can be defined also in terms of the dew-point as *ratio of the saturated vapour pressure at the dew-point to the saturated vapour pressure at the temperature of the atmosphere.*

The relative humidity is generally found by using the first and chiefly the third definitions. Applying the first, the mass of water vapour actually present in a given volume of air is experimentally determined ; then from tables the mass of water vapour required to saturate this volume of air at the temperature of the experiment is taken. The ratio of the first mass to the second gives the relative humidity. When the third definition is used, the dew-point is found by experiment, then the saturation vapour pressures at the dew-point and at the temperature of the experiment are found from tables ; dividing one by the other, the relative humidity is obtained. Tables giving the masses of water vapour necessary for saturation and the saturation vapour pressures at different temperatures have been prepared for ready use.

Hygrometry. The precise measurement of the relative humidity of the atmosphere is called *hygrometry* and the instruments devised for this purpose *hygrometers.* There are many types of hygrometers. We shall here briefly describe the more important ones among them.

Dew-point hygrometer. Many different kinds of the dew-point hygrometer have been designed, but the most reliable one is that due to Regnault ordinarily used in laboratory experiments. It consists of two glass tubes A and B whose lower ends are fitted with silver thimbles S S and upper ends closed with corks. They are mounted side by side. One of them (A) is cooled by placing some ether in it and drawing air through the ether with the help of an aspirator and a narrow glass tube G. The other (B) is kept at room temperature.

The dew-point is observed with a thermometer inserted in the ether, *i.e.*, the temperature at which dew deposits on the surface of the cold thimble and makes it appear cloudy, taking care that the observer's breath does not affect the thimble. Closing the aspirator, the thermometer is again read just when the surface of the thimble clears up. The mean of the two thermometer readings is taken as the dew-point. The purpose of the other tube (B) is to enable the observer to detect easily the deposit of dew on the cold thimble by comparing its surface with a standard silver surface. The thermometer inserted in it serves to read the temperature of the air. Knowing thus the dew-point and the actual temperature of the air, the relative humidity can be calculated with the use of tables, as stated above.

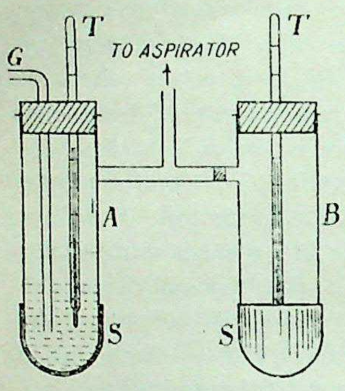


Fig. 93. Regnault's hygrometer.

Wet and dry bulb hygrometer. This instrument is extremely simple to manipulate and hence is widely used in meteorology and industry. It consists of two thermometers mounted on the same board. (Fig. 94). One of them is simply exposed to the air (the dry bulb thermometer) while the other has its bulb enclosed in a piece of wet muslin which is kept saturated with water vapour by means of a cotton wick dipped in a small reservoir of water (the wet bulb thermometer). The dry bulb gives the temperature of the air, while the wet bulb usually gives a lower temperature, due to the continuous evaporation of the water from the muslin surrounding it, the latent heat involved being absorbed from the bulb itself.

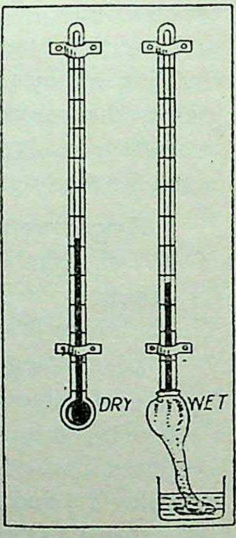


Fig. 94. Wet and dry bulb hygrometer.

Empirical tables are constructed connecting the dew-point with the difference in readings of the two thermometers. Knowing thus the dew-point and the temperature of the air, the relative humidity can be obtained. The greater the relative humidity the slower will be the evaporation on the wet bulb and hence the less the difference in temperature between the wet and dry bulbs. If the relative humidity is cent per cent, no evaporation will occur and the difference in temperature will be zero. These considerations justify the validity of the empirical tables.

In the modern form of the instrument known as the *ventilated wet and dry bulb hygrometer*, special precautions are taken against the current of air flowing past the wet bulb which affects its reading below a certain rate.

Chemical hygrometer. In this device a known volume of air is drawn through drying tubes containing chemicals which absorb all the water vapour in it. The consequent increase in weight of the drying tubes gives the mass of water vapour present in the air. Knowing the mass of water vapour required to saturate the same volume of air at the same temperature from Tables, the relative humidity can be found. Although this method is quite accurate and may be used as a standard to calibrate other hygrometers, it is tedious and cumbersome and hence seldom used for practical purposes.

Hair hygrometer. This type of hygrometer, invented by Saussure in 1783, is very much used in meteorological work as a convenient and easily portable instrument. It is based on the facts that hair free from grease is hygroscopic and when a piece of hair kept under tension absorbs moisture its length increases slightly. Further investigations have shown that this change is approximately proportional to the change in the relative humidity of the atmosphere, within certain limits. A simple type of hair hygrometer is shown in Fig. 95. A long strand of human hair carefully cleaned from all oily matter is kept suitably stretched. The small change in length caused by the change in humidity of the air is magnified by suitable levers to function a pointer moving over a calibrated scale, giving the relative humidity from 0 to 100.

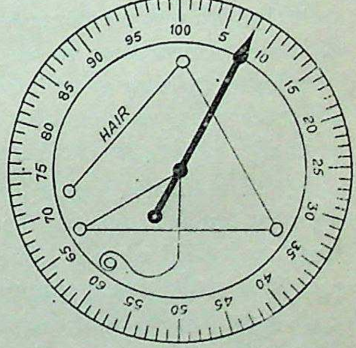


Fig. 95. Hair hygrometer.

The instrument thus gives direct and quick readings of relative humidity ; it can also be arranged to give continuous records. It has, however, a number of drawbacks. It has to be standardised by comparison with a dew-point hygrometer and the calibration has to be checked at frequent intervals to make the readings reliable; even then, the indications are accurate only to about five per cent.

Hygrometry has many practical applications in meteorology and chiefly in industry. In meteorological stations, measurements of relative humidity are made regularly both at ground level and at high altitudes in aeroplanes and the data obtained are used in *weather forecasting*. Normally the atmosphere is not saturated with water vapour; but when it is cooled due to some cause or other, the water vapour actually present may become sufficient to saturate it at a lower temperature; any further fall of temperature results in the condensation of the saturated vapour. Thus, during the day objects on the surface of the earth and the air in contact with them are heated by direct radiation and generally contain a good amount of water vapour. During the night cooling takes place and bodies which radiate well cool quickly. As a consequence the air in contact with these bodies cools also, even down to the dew-point; if further cooling occurs, a portion of the water vapour in the cooled air deposits on objects in the form of *dew*; if the saturated water vapour condenses on dust-particles acting as nuclei in the air close to the earth *mist* or *fog* is formed. During a cold and calm night, cold air from the hills runs down to the valley below and cools the air there to such an extent that its water vapour is condensed into a thick mist. Such mists are seen to form over marshy ground at about sunset on some clear evenings; by early morning the mist may fill the entire valley. The presence of hygroscopic dust particles such as those of soot from the chimneys of factories seems to be necessary for the formation of fog.

Mists formed higher up in the atmosphere, where even electric charges can act as nuclei for condensation of the supersaturated vapour, are called *clouds*. The humid air from the plains driven by winds towards high mountains finds itself obstructed there and hence rushes up the cool sides of the mountains to the higher atmosphere. Due to the low pressure there, the air expands quickly which causes considerable cooling. This is a typical case of cloud formation; but clouds show a great variety of forms according to the different conditions under which they are formed. The case described above forms huge clouds which are known as *cumulus clouds*. Another type, known as *stratus clouds*, is formed when currents of air at different temperatures meet and the layers in contact become regions of condensation. At great heights where the temperature is very low, the vapour condenses into minute ice crystals forming what are known as *cirrus* clouds. The dark rain clouds of cumulus like structure are called *nimbus clouds.* If the lower layers of the upper atmosphere are saturated, the small cloud particles unite together into drops and fall as *rain.* If the cold is sufficiently intense to freeze the minute cloud particles before they coalesce into rain drops, a fall of *snow* occurs. If the rain drops so formed are frozen immediately, *hail* results.

The major important applications of hygrometry are found in industry, chiefly textiles and seasoning of timber. When the atmosphere is nearly saturated with water vapour, as on a calm wet day, the weather is found "sultry" or "muggy", since evaporation of the perspiration from our bodies cannot easily take place under such conditions. Such an oppressive, humid, atmosphere, although bad for health, is required in cotton mills and weaving factories, since if the humidity becomes too low the cotton fibres get electrified by friction and do not spin satisfactorily, with the result that the thread becomes uneven and the "fly waste" is greatly increased. Hence special precautions are taken in such places in order to keep the humidity of the air within useful and hygienic limits.

Seasoning of timber, which takes ordinarily two to three years in the nutural process, can now be achieved artificially within two to three weeks. The process consists in placing the timber in a seasoning kiln, whose temperature and humidity are taken through a series of changes, which season the wood quickly, without however impairing its physical or structural properties.

SUBLIMATION

As already mentioned, *sublimation* is the change of a solid to the vapour state without the intermediate liquid state and the reverse process of passing through direct condensation of vapour to solid is called *hoar-frost.* Under normal conditions of pressure, solids like camphor, iodine, arsenic, etc. do not melt when heated, but "*sublime*". But the process is not peculiar to a few substances alone, but occurs in a smaller or greater measure for all substances. Thus for instance, even ice has an envelope of vapour, which exerts a very small pressure. As a matter of fact, all solid substances possess a finite vapour pressure even at ordinary temperatures. Only we do not notice it when it is too small, but it can be measured with a delicate apparatus.

The phenomenon can be explained as follows. A substance boils at a temperature at which its saturated vapour pressure in equal to the external pressure. If, at a particular temperature, the saturated vapour pressure of a solid substance is greater than the external atmospheric pressure, then the liquid, even if formed, will immediately vaporise, which gives the impression of the absence of the liquid state and of the direct passage of the solid to the vapour state. If, however, the external pressure be sufficiently raised, the solid can be melted into liquid. Thus, camphor, which sublimes under normal pressure, can be melted under sufficiently high external pressure. Hence, a substance sublimes only when the boiling point at atmospheric pressure is less than the melting point ; by increasing the external pressure the boiling point can be raised above the melting point, when the substance will melt first and then vaporise in the usual way.

TRIPLE POINT

When an enclosure is filled with a substance which is partly in the liquid state and partly in the state of saturated vapour, the vapour pressure is a function of temperature alone, as already stated. Hence the relation between saturation vapour pressure and temperature may be represented by a curve PS. (Fig. 96). In the case of water, the curve is called the *steam line*. Since the boiling point rises with the pressure, the curve will have a *positive slope*. Corresponding to any point on this curve, water will just boil, *i.e.*, will exist in equilibrium as liquid and vapour. For any point above the curve water is entirely in the liquid state and for any point below the curve it is entirely in the vapour state. This can be established in a simple manner as follows :—

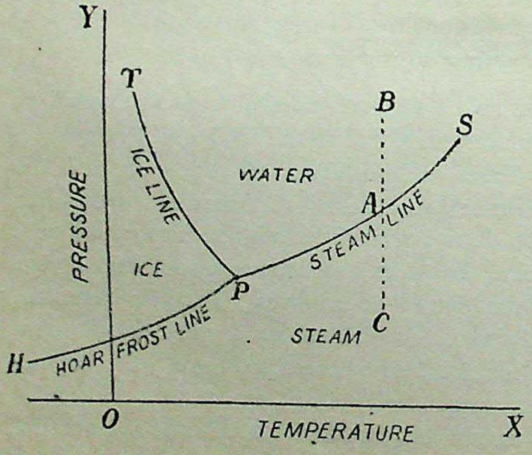


Fig. 96. Triple point for water.

Considering any point A on the curve, let B be another point vertically above A. Corresponding to B, the substance is at the same temperature as at A, but the pressure is greater. The boiling point corresponding to the higher pressure at B will therefore be greater than the temperature represented by both A and B. Hence the substance can exist only as liquid under conditions defined by B. In a similar manner it can be shown that for all points above the curve the substance exists only as liquid (water).

Considering a point C vertically below A, the pressure is lower though the temperature is the same as at A. Hence the boiling point corresponding to C will be lower than the temperature represented by it, which means that at C the substance is at a temperature higher than its boiling point and can therefore exist only as vapour. The same line of reasoning can be used to show that for all points below the curve, the substance remains only as vapour (steam).

If an enclosure contains the substance partly liquid, partly solid and if the two states are in equilibrium, the temperature of the mixture is that at which the solid melts under the pressure within the enclosure. This pressure also is dependent on temperature since the melting point is lowered by increase of pressure. This relation between pressure and melting point can be represented graphically and in the case of water the curve PT (Fig. 96) thus obtained is called the *ice line*, which is *steep*, since the depression of the freezing point is small even for large pressures and has a *negative slope*, since the melting point of ice is lowered by increase of pressure. Similar curves will be obtained for substances which expand on solidification, like ice. Corresponding to all points on the curve the substance will be just melting, *i.e.*, will exist in equilibrium as solid and liquid. For any point above the curve the substance is entirely in the liquid state (water) and for any point below the curve, entirely in the solid state (ice), which can be proved by reasoning similar to the one used in the case of the *steam line*.

Finally a substance can exist in the solid and vapour states together in equilibrium and the curve PH (Fig. 96) representing the relation between pressure and temperature in such a case is called the *hoar frost line* for water. It has a *positive slope* and is nearly horizontal. It can be easily shown, as in the previous cases, that the substance can exist only as solid (ice) corresponding to condition represented by points above the curve, as vapour (steam) below the curve, and in equilibrium as solid and vapour on the curve itself.

When all the three curves are drawn on the same graph paper they are found to meet at a single point P which is called the *triple point*. It may be defined as a *point representing a particular tempera-*

ture and pressure, when a substance exists simultaneously in the solid, liquid and vapour states in equilibrium, in the same enclosure, without any change in their relative proportions.

That the three curves should meet at a point can be established by a very simple reasoning as follows :—

If the three curves do not meet at a single point, let them intersect each other forming a small triangle ABC, as shown in Fig. 97. Then, since the space ABC is above the steam line, points in it must correspond, in a state of equilibrium, to the existence of water alone. On the other hand, since ABC is below the hoar frost line, points in it must also correspond to the existence of vapour alone. Again, since ABC is below the ice line, points in it will have to correspond to the existence of ice alone. Thus the assumption that the three curves do not meet at a single point leads to three different and mutually contradictory conclusions.

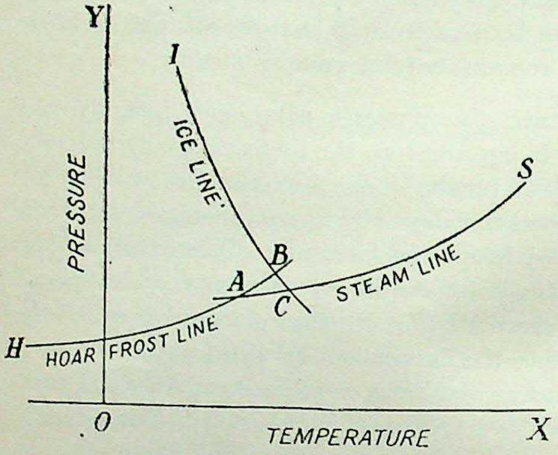


Fig. 97.

That the three curves must intersect in a common point can be established also from the principles of thermodynamics.

Regnault, as a result of his experiments, concluded that the hoar frost line was a continuation of the steam line. But later, Kirchhoff showed that the two lines were distinct curves, meeting each other at an angle.

For substances other than water the three curves are known as *vaporisation line, fusion line* and *sublimation line* respectively. In the case of substances which contract on solidification unlike water, the fusion line has a positive slope, as shown in Fig. 98.

The triple point of a substance like water which expands on solidification is above its melting point at normal pressure and the substance cannot exist in the solid state above the triple point. The triple point of a substance which contracts on solidification is below its melting point under normal pressure and the substance cannot exist in the liquid state above the triple point. These differences can be easily visualised by a comparison of Figs. 96 and 98.

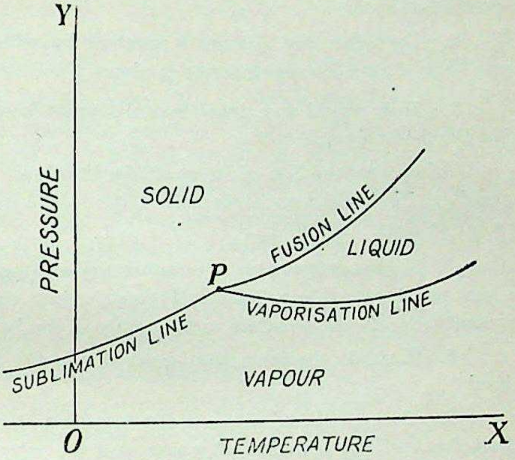


Fig. 98.

Pressure and temperature of the triple point of water can be easily calculated by considering the coordinates of the point of intersection of the ice line with the steam line.

Let p and t be the pressure and temperature of the triple point.

The melting point of ice at normal pressure of 760 m.m. = 0°C.

The melting point of ice is lowered by 0·0072°C for every atmosphere (760 mm.) increase of pressure, as experimentally found.

∴ Under a pressure of p mm. ice will melt at

$$\left(0{\cdot}0072 - \frac{\cdot 0072}{760}\, p \right)^{\circ}\mathrm{C} = t \qquad \ldots(1)$$

From tables we have

the saturated vapour pressure at 0°C = 4·60 mm.

the saturated vapour pressure at 1°C = 4·94 mm.

∴ The increase in vapour pressure per °C = 0·34 mm.

Hence the saturated vapour pressure at t°C is

$$(4{\cdot}60 + 0{\cdot}34t) \text{ mm.} = p \qquad \ldots(2)$$

Solving (1) and (2), the value of p and t are obtained :—

From (2) $\qquad p = 4{\cdot}6 + {\cdot}34t$

Or $\qquad t = \dfrac{p - 4{\cdot}6}{\cdot 34}$

Substituting this in (1)

$$\frac{p - 4{\cdot}6}{\cdot 34} = \left(\cdot 0072 - \frac{\cdot 0072}{760}\, p \right)$$

∴ $\qquad p = 4{\cdot}6024$ mm.

From (2) $(4{\cdot}60 + 0{\cdot}34t) = 4{\cdot}6024$; $\qquad \therefore\ t = 0{\cdot}007156$°C.

QUESTIONS

1. Define latent heat of ice. Explain how it can be used for estimating quantities of heat. (*Madras University*)

2. Describe and discuss a method by which you could determine the latent heat of a metal which melts at about 200°C. (*Oxford*)

3. How would you determine the latent heat of vaporisation of a liquid using Berthelot's spiral ?

A boy eats 0·3 Kg. of ice at 0°C in 10 mins. What horse power does he expend, if his body temperature is 98·4F ? (746 watts = 1 H.P., L of ice = 80 cals./gm.) **Ans.** 0·0187 H.P. (*Madras University*)

4. Define latent heat of evaporation of liquids and describe how it can be measured accurately. State Trouton's law connecting the latent heat of evaporation with the absolute temperature of the boiling point. (*Cambridge*)

5. Explain the term 'total heat of steam'. How is this quantity determined ? (*Madras University*)

6. Give a critical account of Henning's electrical method of finding the latent heat of vaporisation of water, and say why you consider it superior to Berthelot's method.

7. Distinguish between internal and external latent heats of steam. Given that 1 gm. of saturated steam at 100°C and 760 m.m. pressure occupies 1560 c.c., calculate the internal latent heat of steam. **Ans.** 498·4 cals./gm. (*Madras University*)

8. An electric current of 0·75 amp. is passed for 30 mins. through a coil of wire of 12·4 ohms resistance immersed in benzene maintained at its boiling point ; 29·85 gms. of benzene are found to have vaporised. Calculate the latent heat of vaporisation of benzene. Describe the apparatus you would set up in order to obtain observations of this kind. **Ans.** 100·5 cals./gm. (*Cambridge*)

9. Give an account of surfusion, and show how it has been applied to the determination of the freezing point of solutions.

10. How can the effect of pressure on the melting point of a solid be investigated theoretically ? Describe any experiments which have been performed to test the predictions.

11. Discuss the phenomenon of regelation and give some examples of it.

12. Assuming the fact concerning saturated vapours, discuss the physical properties underlying ebullition and state how far your predictions are verified by experiment.

13. State the facts about superheating and boiling by bumping and show how they can be explained.

14. Describe and explain the effect of pressure on the boiling point of a liquid. (*Tripos*)

15. Explain clearly what is meant by a saturated vapour. Describe how you would measure the vapour pressure of water (*a*) at temperatures below its freezing point, (*b*) at temperatures above its boiling point. Emphasise in each case the physical principles on which the method is based.

16. What are the principal differences between saturated and unsaturated vapours ? How would you determine the pressure of saturated water vapour at temperatures between 40°C and 110°C ? *(Madras University ; Cambridge)*

17. How would you determine the vapour pressure of a liquid above its normal boiling point ? Explain how clouds are formed by the mixing of warm moist air with cold moist air. *(Allahabad University)*

18. Show how the saturated pressure of a vapour in contact with a liquid depends on the curvature of the liquid surface. Explain the conditions essential for (*a*) supersaturation of a vapour (*b*) super cooling of a liquid.

19. A mixture of a gas and a saturated vapour is contained in a closed space. How will the pressure of the mixture vary (*a*) when the temperature is changed and the volume is kept constant, (*b*) when the volume is changed and the temperature is kept constant ? *(Oxford and Cambridge)*

20. Describe a method of determining the vapour density of a volatile liquid and explain the theory of your method. *(Dacca University)*

21. What is meant by (*a*) relative humidity, (*b*) dew-point ?

Describe in detail the modern form of Regnault's hygrometer and discuss the part it plays in practical measurement of relative humidity.

22. Explain the general principles underlying the employment of a wet and dry bulb hygrometer for determining the hygrometric state of the atmosphere explaining what is meant by hygrometric state.

23. Describe the hair hygrometer and state the industrial application of hygrometry.

24. Define triple point and show that it is unique for a given substance.

Calculate the temperature and pressure of the triple point, given that the lowering of M.P. of ice is 0·0072°C per atmosphere ; pessure of saturated vapour at 0°C = 4·6 mm. and at 1°C=4·94 mm. of mercury.

(Allahabad University 1942 ; Madras University)

25. What is meant by the triple point of a substance ? How is it affected by pressure ?

26. What are *ice line, steam line* and *hoar frost line* ? Show that they meet at a point. Draw a diagram showing the general shape of the isothermals above and below the triple point of a substance which (*a*) expands on melting, (*b*) contracts on melting. Give an explanation of your diagram.

CHAPTER V

TRANSFERENCE OF HEAT

CONDUCTION, CONVECTION, RADIATION

Introduction. Heat is transferred or propagated by three distinct processes, *viz.*, conduction, convection and radiation.

The fact that heat can be *conducted* through the material of a body is well known. For example, when a metal rod is heated at one end, the heat gradually spreads along the rod and the other end also becomes hot after some time. The power of transmitting heat in this manner is possessed by all substances, solids, liquids and gases, to a varying degree, and the process is called *conduction.* Maxwell defined it as "the flow of heat through an unequally heated body from places of higher to places of lower temperature". It is to be noted that in this kind of propagation of heat, although the material of the body takes an active part, there is no visible movement of the material itself.

Another way of transference of heat is readily observed when say a beaker of water is heated by a flame placed below it. The process can be followed if some crystals of potassium permanganate are placed at the bottom of the beaker before heating it. Water rises up from the bottom and then curls down the sides, which is made visible by the red colour acquired by the water from the crystals. This shows that the heated particles move from the bottom to the top, while the cooler particles go down to be heated and then go up. The power of transmitting heat in this way by the actual motion of heated particles, unlike in the case of conduction, is possessed by liquids and gases and is known as *convection.* Maxwell defined it as "the motion of the hot body itself carrying its heat with it".

There is a third way of transference of heat, which is made quite evident from the manner we receive heat from the sun. Although the sun is millions of miles away from the earth and there is only empty space with no material medium for the greater part of the distance, yet heat from the sun reaches us with the enormous velocity of light. This process cannot be either conduction or convection, which are comparatively slow and require an intervening material medium. It is called *radiation* and Maxwell defined it as follows : "In radiation, the hotter body loses heat and the colder body receives heat by means of a process occurring in some intervening medium which does not itself thereby become hot." In so defining radiation, although he seems to admit some intervening medium, he is careful not to assert whether that medium is empty or filled with the so-called *ether*. We know for certain that radiation takes place even in the best vacuum, *i.e.*, where there is no matter, solid, liquid or gas. At any rate in this process the intervening medium, if any, does not take an active part, by itself getting heated, as in the case of conduction and convection.

In this chapter we shall study these three modes of propagation of heat, more in detail with quantitative definitions and measurements, with illustrative examples and practical applications and with further elucidation of the inner mechanism involved.

CONDUCTION

Definition of thermal conductivity. Fourier, who was the first to study the phenomenon of heat conduction in a systematic manner and place it on a sound mathematical basis, gave a precise definition of conductivity, by the following line of reasoning :—

Let a rod of uniform cross-section be heated at one end ; heat starts flowing from the hot end to the cold along the rod. Considering a thin element of the rod at some distance from the hot end, with faces perpendicular to the length of the rod, the face nearer the hot end will be obviously at a higher temperature than the other face farther away ; more heat enters the element than leaves it. The amount of heat thus left with the element is used partly to warm up the element and partly in radiation from the surface of the element. As the element gets hotter, the portion radiated to the surrounding increases, while the portion spent in heating the element assumes a practically constant value. Soon a stage is reached, when the amount of heat radiated becomes exactly equal to the excess left with the element over and above the heat absorbed to raise its temperature which has now reached a constant value depending on the thermal capacity of the material. Such a stage is known as the *steady state*, when the temperature of each element in the rod attains a constant value, which decreases gradually from the hot to the cold end. In other words, when the steady state is reached the temperature of a given point in the rod is a function of its distance from the hot end and is independent of time. It may be noted also that in the steady state, the heat flow and the temperature distribution along the rod become independent of the specific heat of the material of the rod, since no further change in temperature takes place at any point.

Let θ_1 and θ_2 be the constant temperatures of the two faces of an element of the rod of thickness l and of cross-sectional area A, in the steady state. It is found experimentally that the amount of heat Q flowing through the element in a time t is proportional directly to A, $(\theta_1 - \theta_2)$ and t, and inversely to l. Hence

$$Q = K \frac{A (\theta_1 - \theta_2) t}{l} \qquad \dots (1)$$

where K is a constant whose value depends upon the nature of the material of the rod and is called the *coefficient of thermal conductivity* or simply *thermal conductivity*.

If $A = 1$, $(\theta_1 - \theta_2) = 1$, $t = 1$ and $l = 1$, $Q = K$; this enables the coefficient of thermal conductivity to be defined as follows :—

The quantity of heat flowing per second through unit area of cross-section of an element of the material, of unit thickness, when the difference of temperature between its faces is unity.

The quantity $\dfrac{\theta_1 - \theta_2}{l}$, which represents the rate of fall of temperature with distance in the direction of the heat flow, is known as the *temperature gradient*. As there are many cases in which the temperature gradient is not uniform, it becomes necessary to reduce the quantity $\dfrac{\theta_1 - \theta_2}{l}$ to the limit value $\dfrac{d\theta}{dx}$, and rewrite relation (1) as :

$$Q = - K A \frac{d\theta}{dx} \, . \, t \qquad \dots (2)$$

This relation is of fundamental importance in the theory of heat conduction. Usually a —ve sign is attached to the R.H.S. of the equation, to indicate that $\dfrac{d\theta}{dx}$ is —ve, since it represents the rate of fall of temperature with distance in the direction of the heat flow.

In analogy with electrical resistance, the reciprocal of the thermal conductivity (1/K) is called *thermal resistance*.

The *units in which* K *is measured* in the C.G.S. system are the calories per sec. per sq. cm. of cross-sectional area for a temperature gradient of 1°C per cm.

Dimensions of K. Expressing relation (2) as

$$K = \frac{Q \,.\, dx}{A \,.\, d\theta \,.\, t}$$

since Q is a form of energy, its dimensions are $M^1L^2T^{-2}$; dx is a length. Hence

$$[K] = \frac{M^1L^2T^{-2} \,.\, L}{L^2 \,.\, \theta \,.\, T} = M^1L^1T^{-3}\,\theta^{-1}$$

Thermal diffusivity or thermometric conductivity. Before the steady state is reached, the rate at which the rod gets heated will not be the same for all materials, for it will depend not only on the thermal conductivity but also on the thermal capacity. The rate at which the temperature of any part of the rod changes is determined by a quantity which has been called *thermal diffusivity* by Lord Kelvin and *thermometric conductivity* by Maxwell and is given by the *ratio of the thermal conductivity to the thermal capacity per unit volume of the material of the rod.* If s is the specific heat and ρ the density (mass per unit volume) of the material of the rod, then the *diffusivity* (h) is given by relation

$$h = \frac{K}{\rho s} \qquad \dots (3)$$

This relation will be established presently. In all problems of thermal conductivity, the steady state is presumed, unless the contrary is expressly stated, in which case the thermal diffusivity and not the thermal conductivity has to be taken into account.

Theoretical investigation. We shall now study a few important cases of conductive flow of heat and derive the respective theoretical relations, which will be found useful in the experimental determination of thermal conductivity by different methods.

(1) **Rectilinear flow of heat along a bar.** Considering a long metal bar heated at one end, let us suppose that the bar lies along the X-axis of a set of co-ordinates, whose origin is at the hot end. (Fig. 99.)

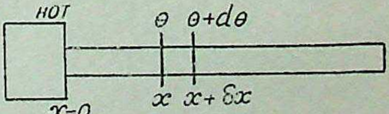


Fig. 99.

Consider two parallel planes perpendicular to the length of the bar at a distance x and $x + \delta x$ from the hot end. Let θ be the excess of temperature of the plane at x above the surrounding and

$\frac{d\theta}{dx}$ the temperature gradient. Then, the excess of temperature of the plane at $x + \delta x$ is $\theta + \frac{d\theta}{dx}\,\delta x$ and the temperature gradient there is $\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}\,\delta x\right)$.

If Q_1 and Q_2 be the quantities of heat that enter the plane at x and leave the plane at $(x + \delta x)$ per second respectively,

$$Q_1 = -\,K\,A\,\frac{d\theta}{dx},$$

where K is the thermal conductivity and A the cross-sectional area of the bar,

$$\text{and} \qquad Q_2 = -\,K\,A\,\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}\,\delta x\right)$$

$$= -\,K\,A\left(\frac{d\theta}{dx} + \frac{d^2\theta}{dx^2}\,\delta x\right)$$

Therefore the amount of heat gained per second by the element of thickness δx, bounded by the two planes, is given by

$$Q_1 - Q_2 = -\,K\,A\,\frac{d\theta}{dx} - \left\{-\,K\,A\left(\frac{d\theta}{dx} + \frac{d^2\theta}{dx^2}\,\delta x\right)\right\}$$

$$= K\,A\,\frac{d^2\theta}{dx^2}\,\delta x. \qquad \ldots (1)$$

Before the steady state is reached, this heat will be spent partly in raising the temperature of the element and partly in radiation from the surface of the element. If $\frac{d\theta}{dt}$ is the rate of rise in temperature of the element, ρ the density and s the specific heat of the material, the heat required to raise the temperature of the element at the above stated rate

$$= A\,.\,\delta x\,.\,\rho\,.\,s\,.\,\frac{d\theta}{dt}$$

If p is the perimeter of the element, the surface area of the element $= p\,.\,\delta x$. If E is the emissivity or radiating power of the surface and θ the average excess of temperature of the element, assuming Newton's law of cooling, the heat radiated by the element, per second $= E\,.\,p\,.\,\delta x\,.\,\theta$.

$$\text{Hence } K\,A.\,\frac{d^2x}{dx^2}\,\delta x = A\,.\,\delta x\,.\,\rho\,.\,s\,.\,\frac{d\theta}{dt} + E\,.\,p\,.\,\delta x\,.\,\theta$$

Dividing by KA δx throughout,

$$\frac{d^2\theta}{dx^2} = \frac{\rho s}{\text{K}} \cdot \frac{d\theta}{dt} + \frac{\text{E}p}{\text{KA}}\,\theta \qquad \dots (2)$$

This is the standard equation for unidirectional flow of heat and any problem in thermal conduction along a bar can be analysed by the solution of this differential equation taking into account the actual conditions of the problem.

Supposing the heat lost by radiation is negligible, equation (2) reduces to

$$\frac{d^2\theta}{dx^2} = \frac{\rho s}{\text{K}} \cdot \frac{d\theta}{dt}$$

or

$$\frac{d\theta}{dt} = \frac{\text{K}}{\rho s} \cdot \frac{d^2\theta}{dx^2} = h \cdot \frac{d^2\theta}{dx^2} \qquad \dots (3)$$

where $h = \dfrac{\text{K}}{\rho s}$ is the *diffusivity*, which determines the rate at which temperature changes take place in the bar, as already stated.

After the steady state is reached, the element no longer rises in temperature ; hence $\dfrac{d\theta}{dt} = 0$. Then the relation (2) reduces to

$$\frac{d^2\theta}{dx^2} = \frac{\text{E}p}{\text{KA}} \cdot \theta = \mu^2 \,.\, \theta \qquad \dots (4)$$

where

$$\mu^2 = \frac{\text{E}p}{\text{KA}}$$

Since equation (4) is a differential equation of the second degree, its general solution is

$$\theta = \text{A}e^{\mu x} + \text{B}e^{-\mu x} \qquad \dots (5)$$

where A and B are two constants, which can be determined from the boundary conditions. Let the excess of temperature of the hot end above the surrounding be θ_0°C and that of the cold end be zero, which is rigorously true only when the bar is of infinite length, but roughly realised when the bar is long enough for the cold end to be nearly at the room temperature. Then,

when $x = 0$, $\theta = \theta_0$°C and when $x = \infty$, $\theta = 0$.

Substituting these values in equation (5)

$$\theta_0 = \text{A} + \text{B}$$

and

$$0 = \text{A}e^{\infty}$$

But e^{∞} is not equal to zero ; hence $A = 0$

$$\therefore \qquad B = \theta_0$$

$$\text{and} \qquad \theta = \theta_0 e^{-\mu x} \qquad \dots (6)$$

This relation (6) gives the excess of temperature at any point x along the bar, *exposed to radiation*, after the steady state is reached which, we see, is an exponential function of the distance x of the point from the hot end and is independent of time.

If the bar is covered, so that radiation loss is negligible, $E = 0$, and hence $\mu^2 = 0$, so that $\dfrac{d^2\theta}{dx^2} = 0$.

Integrating twice,

$$\theta = A' x + B'$$

where A' and B' are constants which can be determined from the boundary conditions.

When $x = 0$, $\theta = \theta_0$; $\quad \therefore \quad \theta_0 = B'$.

When $x = l$, where l is the known length of the whole bar or a part of it, let $\theta = \theta_1$.

Then $\theta_1 = A'l + B'$ or $A' = \dfrac{\theta_1 - \theta_0}{l} = -\dfrac{\theta_0 - \theta_1}{l}$.

Substituting these values of A' and B'

$$\theta = \theta_0 - \frac{\theta_0 - \theta_1}{l} \cdot x \qquad \dots (7)$$

This relation (7) gives the excess of temperature at any point x along the bar, covered and hence prevented from radiating.

(2) **Three dimensional flow of heat.** So far we have confined our attention to the propagation of heat in one direction only. The general case, in which the flow of heat may take place in any direction, may be treated in a similar manner, by amplifying the ideas stated above to cover the conduction of heat in three dimensions. The general equation of conduction thus obtained is of the form

$$K\left(\frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2}\right) = \rho s \frac{d\theta}{dt}$$

$$\text{or} \qquad h \nabla^2 \theta = \frac{d\theta}{dt} \qquad \dots (8)$$

where h is the diffusivity and ∇ the Laplacian operator.

After *the steady state* is reached, $\dfrac{d\theta}{dt} = 0$, so that we have

$$\nabla^2 \theta = 0 \qquad \dots (9)$$

The simplest case of heat conduction in three dimensions is that of a sphere with its centre being heated. The thermal conductivity has been determined by using the material in the form of a spherical shell, as we shall see below. We shall here study this case theoretically and derive the appropriate equation.

✓(3) **Radial flow of heat in a spherical shell.** Assuming that the source of heat is placed at the centre of the spherical shell, the isothermal surfaces in the shell are spherical. Considering a spherical surface of radius r, (Fig. 100), the flow of heat across it per sec. is $- K. 4\pi r^2 \frac{d\theta}{dr}$. This must be equal to the amount of energy Q supplied by the source at the centre per sec.

$$\therefore \quad Q = - K. 4\, \pi\, r^2 \frac{d\theta}{dr}$$

$$\text{Or } d\theta = - \frac{Q}{4\pi K} \frac{dr}{r^2}$$

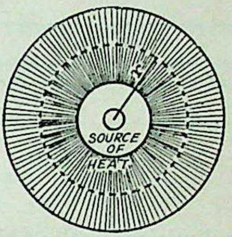


Fig. 100.

On integrating, (remembering that Q is independent of r)

$$\theta = \frac{Q}{4\pi K} \cdot \frac{1}{r} + A \qquad \text{... (1)}$$

where A is a constant of integration.

If the two surfaces of the shell of radii r_1 and r_2 acquire temperature θ_1 and θ_2 in the steady state, we have

$$\theta_1 = \frac{Q}{4\pi K} \cdot \frac{1}{r_1} + A \text{ and } \theta_2 = \frac{Q}{4\pi K} \cdot \frac{1}{r_2} + A \qquad \text{... (2)}$$

Subtracting one from the other and rearranging

$$Q = \frac{4\pi K\, (\theta_1 - \theta_2)\, r_1 r_2}{r_2 - r_1} \qquad \text{... (3)}$$

Using this relation (3), K can be calculated from the known values of Q, θ_1, $\theta.$, r_1 and r_2.

Solving the simultaneous equations for Q and A and substituting these values of Q and A in (1), the temperature distribution in the spherical shell can be obtained. The temperature θ of the spherical surface of radius r is given by

$$\theta = \frac{1}{r_1 - r_1} \left\{ (r_2\theta_2 - r_1\theta_1) + \frac{(\theta_1 - \theta_2)\, r_1 r_2}{r} \right\} \qquad \text{... (4)}$$

(4) Flow of heat across the walls of a cylindrical tube. Consider a cylindrical tube of internal radius r_1, external radius r_2 and length l, which has an electrically heated wire along its axis (Fig. 101). It is assumed that heat is flowing radially across the walls of the tube, and when the steady state is reached, let θ_1 and θ_2 be the constant temperatures of the inner and outer surfaces of the tube respectively.

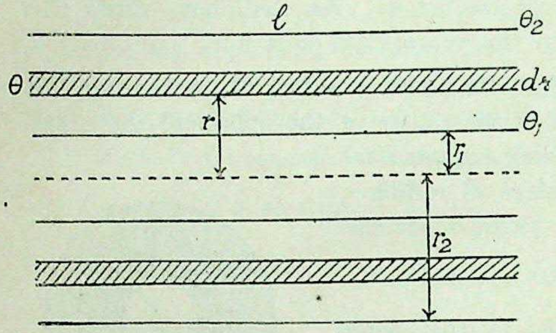


Fig. 101.

Considering a thin cylindrical shell of thickness dr at a distance r from the axis, let its temperature be θ. The amount of heat Q flowing through this shell per second is given by

$$Q = -\text{KA} \cdot \frac{d\theta}{dr} = -\text{K} \cdot 2\pi rl \cdot \frac{d\theta}{dr} \qquad \ldots (1)$$

since A, the area of the surface of the shell $= 2\pi rl$.

The above relation can be written as

$$Q\,\frac{dr}{r} = -\text{K}\, 2\,\pi\, l\, d\theta$$

Integrating both sides between their respective limits, we have

$$Q \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi \text{K} l \int_{\theta_1}^{\theta_2} d\theta$$

Q becomes constant in the steady state, since the quantity of heat flowing per second across any thickness of the cylinder is the same.

$$\therefore \qquad Q \log_e \frac{r_2}{r_1} = 2\pi \text{K} l\,(\theta_1 - \theta_2)$$

$$\text{Or} \qquad \text{K} = \frac{Q \cdot \log_e (r_2/r_1)}{2\,\pi\, l\,(\theta_1 - \theta_2)} \qquad \ldots (2)$$

Hence measuring Q, r_1, r_2, l, θ_1 and θ_2, can be estimated.

The temperature θ of the cylindrical shell at the distance r can be shown to be given by

$$\theta = \frac{1}{\log_e (r_2/r_1)} \left\{ (\theta_1 \log_e r_2 - \theta_2 \log_e r_1) - (\theta_1 - \theta_2) \log_e r \right\} \qquad \ldots (3)$$

Experimental determination of thermal conductivity. Metals, in general, are good conductors of heat, while non-metals, like glass, wood, rubber, etc., are bad conductors. Liquids, in general, are worse conductors of heat than solids, and gases are the worst. Hence, in the study of the experimental determination of thermal conductivity, it is advantageous to deal with the methods devised for solids, liquids and gases separately and in the case of solids to consider good and bad conductors also separately.

CONDUCTIVITY OF SOLIDS

1. Ingen-Hauzs method of comparing the conductivities of different metals. Rods of different metals, but of exactly the same size and shape, electroplated and polished similarly, are fitted into holes on the side of a vessel, as shown in Fig. 102. The portions of the rods projecting outside the vessel are coated uniformly with wax. The vessel is filled with hot water or oil. When a steady state has been attained, it is found that the wax has melted to different lengths on the different rods. Let l_1, l_2, l_3,... denote the lengths up to which the wax has melted on the different rods, θ_0 the temperature of the hot water or oil in the common bath measured above that of the surrounding and θ_m the melting point of wax. Then, using relation (6) on page 242, we have

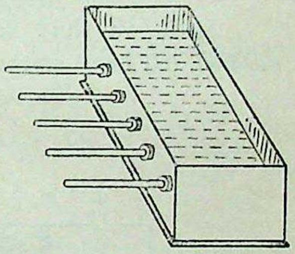


Fig. 102. Ingen Hausz's apparatus.

$$\theta_m = \theta_0 \, e^{-\mu_1 l_3} = \theta_0 \, e^{-\mu_2 l_2} = \theta_0 \, e^{-\mu_3 l_3} = \ldots$$

since θ_m gives the temperature of the point up to which wax has melted in each of the rods.

Hence $$\mu_1 l_1 = \mu_2 l_2 = \mu_3 l_3 = \ldots$$

Substituting the values of μ_1, μ_2, μ_3, etc., we have

$$\left(\frac{\mathrm{E}p}{\mathrm{K_1A}}\right)^{\frac{1}{2}} l_1 = \left(\frac{\mathrm{E}p}{\mathrm{K_2A}}\right)^{\frac{1}{2}} l_2 = \left(\frac{}{\mathrm{K_3A}}\right)^{\frac{1}{2}} l_3 = \ldots$$

where K_1, K_2, K_3, etc., are the conductivities of the rods.

Since the emissivity E, the perimeter p and the cross-sectional area A are the same for all the rods.

$$\frac{l_1}{\sqrt{K_1}} = \frac{l_2}{\sqrt{K_2}} = \frac{l_3}{\sqrt{K_3}} = \ldots$$

Or $$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \ldots \text{ constant}$$

This means that the conductivities of the different rods are directly proportional to the square of the lengths up to which wax has melted on them. Hence, if the conductivity of one of the rods is known, the conductivities of all the others can be calculated. This is an indirect method, not capable of giving accurate results, but can be employed for demonstration purposes.

2. **Determination of thermal conductivity of metals based on the definition.** A number of workers have devised methods of measuring the conductivity of metals which are *good conductors* based on the relation used in the definition of conductivity, *viz.*

$$Q = K A \, . \, \frac{\theta_1 - \theta_2}{l} \, . \, t \qquad (Cf.\ \text{p. } 238)$$

Here we shall describe only three of them, *viz.* (*i*) Searle's method, (*ii*) Lees' method, and (*iii*) Honda and Simidu method.

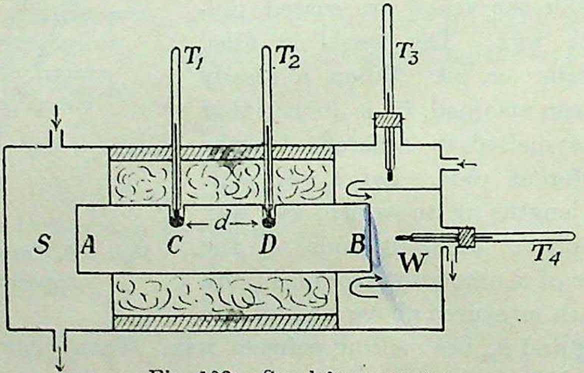


Fig. 103. Searle's apparatus.

Searle's method. This method which is ordinarily used as a laboratory experiment is known also as the '*guard-ring*' method. The apparatus employed is shown in Fig. 103. A cylindrical rod AB of the metal under study, about 30 cm. long and 4 cm. diameter, is used. One end A of it is enclosed in a steam chamber S, while the other end B in another chamber W, through which cold water circulates at a steady rate, as shown in the figure. The temperature of the water at entry and exit are noted by two sensitive thermometers T_3 and T_4. The temperatures at two points along the rod are measured by two other thermometers T_1 and T_2 inserted into holes C and D drilled in the rod and containing a little mercury for good contact. Loss of heat by radiation from the sides of the rod is prevented by covering the rod with felt and enclosing it in a wooden case, this protection being known as the '*guard-ring*'.

Steam is passed through S and water is circulated through W for a pretty long time until the steady state is reached, as indicated by the constant readings of T_1, T_2, T_3 and T_4. It may be necessary to regulate the flow of water in W, so that T_3 and T_4 show a decent and constant difference of temperature in the steady state. The readings θ_1, θ_2, θ_3 and θ_4 of T_1, T_2, T_3 and T_4 respectively are noted. The outflowing water is then collected in a weighed beaker for a given time (t secs.) and the mass m of the water thus collected is found.

The quantity of heat which reaches the end B and is absorbed by the water in t secs. $= m\,(\theta_4 - \theta_3)$. In the steady state, this gives also the quantity of heat Q flowing across any section of the rod in the same time, *i.e.*, t secs.

$$\therefore \qquad Q = m\,(\theta_4 - \theta_3).$$

The temperature gradient $= \dfrac{\theta_1 - \theta_2}{d}$, where d is the distance between the holes in which T_1 and T_2 are inserted.

Using the relation, appropriate to the case, *viz.*

$$Q = m\,(\theta_4 - \theta_3) = K\,A\,\frac{\theta_1 - \theta_2}{d}\,.\,t$$

where A is the cross-sectional area of the rod $= \pi r^2$ (r = radius of the rod), K can be found, since all the other quantities are known.

Lees' method is suited for measuring the conductivity of metals at various temperatures, chiefly low, down to liquid air temperature, whereas the previous method can be used only for fairly high temperature and gives the average conductivity over a fairly wide range of temperature. Lees' apparatus, (Fig. 104), consists of a small rod AB, about 7 cm. long and 0·5 cm. in diameter, fitted in a copper frame C as shown in the figure. The rod is provided with a heater coil H_1 at one end A and two platinum resistance thermometers T_1 and T_2 to measure the temperature at two points in the rod at a known distance d apart. The whole arrangement is mounted inside a Dewar flask D in order to prevent escape of heat from the surface of the rod by radiation. Another heater coil H_2 is wound round the copper frame C in order to maintain the apparatus at any desired temperature.

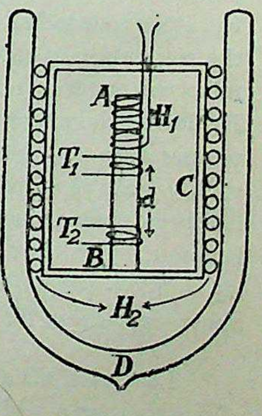


Fig. 104. Lees' apparatus for studying the variation of K with temperature.

The apparatus is first immersed in liquid air till the temperature falls somewhat below the temperature at which the conductivity is to be measured. Then the liquid air is poured out of D and the copper frame is heated with H_2 till the desired temperature is obtained. The end A of the rod is heated by passing a current through the coil H_1, whose current value I and the potential difference E across the coil are measured. The heating is continued for a known time t till the steady state is reached, as indicated by the constant readings θ_1 and θ_2 of the two thermometers T_1 and T_2. Using the relation

$$Q = \frac{EIt}{J} = KA \frac{\theta_1 - \theta_2}{a} . t$$

$$\text{or} \qquad K = \frac{EId}{J\,A\,(\theta_1 - \theta_2)}$$

the thermal conductivity K of the material of the rod can be determined at the temperature chosen.

There is an important *correction* to be made. When the end A of the rod is being heated, the copper frame conducts some of the heat and rises in temperature. This, in turn, reacts on the rod and raises first the temperature of the cold end B and ultimately of the whole rod. On account of this backward flow of heat, the difference in temperature $(\theta_1 - \theta_2)$ will be less than what it would have been, if the steady state had been reached normally. To apply the correction, the resistances of the coils H_1 and H_2 are made equal. Before performing the experiment, the same current which is to be passed through H_1 during the experiment is passed through H_2 and the difference of temperature $d\theta_1$ between T_2 and T_1 (T_2 being now the hotter) in the steady state is noted. The observation is repeated after the current has been passed through H_1 and the new temperature difference $d\theta_2$ is noted. The corrected temperature difference is then given by $(\theta_1 - \theta_2) + (d\theta_1 + d\theta_2)/2$, which is used, instead of $(\theta_1 - \theta_2)$, in the above expression for K.

Lees with his apparatus measured the conductivity of a number of metals over a wide range of temperature, from 18°C to — 170°C, and was able to obtain valuable information about the variation of conductivity with temperature.

Honda and Simidu method. The apparatus is shown in Fig. 105. Two exactly similar plates PP made of the metal under test are arranged symmetrically on opposite sides of an electrical heater H which generates the heat Q. Two cold plates CC maintained at the same temperature are placed on the outer faces of the experimental plates, in order to secure perfect symmetry. With such an arrangement the amount of heat flowing through each plate is Q/2. The experiment is conducted as in the case of a rod and K is found as the average of two sets of readings.

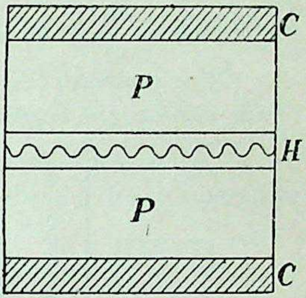


Fig. 105. Honda at Simidu apparatus

3. **Forbes' method.** This is one of the earliest methods used for determining the *absolute conductivity* of metals devised by Forbes.

The *principle* of the method is as follows : A long bar of the metal under test is heated until the steady state is reached, when the amount of heat passing through any section B of the bar at a distance x from the hot end is equal to the heat lost by radiation by the bar beyond the section B chosen. In the steady state, according to theory, the amount of heat passing per second through a section B at a distance x from the hot end $= \mathrm{KA}\left(\frac{d\theta}{dx}\right)_{\mathrm{B}}$, where K is the conductivity, A the cross-sectional area and $\left(\frac{d\theta}{dx}\right)_{\mathrm{B}}$ the temperature gradient at B.

The amount of heat lost in radiation by the bar beyond the section B $= \int_{\mathrm{B}}^{end} \rho\, \mathrm{A}\, s \frac{d\theta}{dt}\, dx$, where ρ and s are the density and specific heat of the material of the bar and $\frac{d\theta}{dt}$ is the rate of change of temperature.

$$\therefore \qquad \mathrm{K\,A}\left(\frac{d\theta}{dx}\right)_{\mathrm{B}} = \int_{\mathrm{B}}^{end} \rho\, \mathrm{A}\, s\, \frac{d\theta}{dt}\, dx$$

Or

$$\mathrm{K} = \frac{\rho s \int_{\mathrm{B}}^{end} \frac{d\theta}{dt}}{\left(\frac{d\theta}{dx}\right)_{\mathrm{B}}} \qquad \ldots(i)$$

Hence, in order to determine K, $\left(\frac{d\theta}{dx}\right)_{\mathrm{B}}$ and $\int_{\mathrm{B}}^{end} \frac{d\theta}{dt}\, dx$ are to be found, since ρ and s are assumed. The experiment therefore consists of two parts, *viz. static* to determine $\left(\dfrac{d\theta}{dx}\right)_B$ and *dynamic* to determine $\left(\dfrac{d\theta}{dt}\right)$ and thence $\displaystyle\int_B^{end} \frac{d\theta}{dt}\, dx$.

The *apparatus* (Fig. 106) consists of a long metallic bar of uniform section, the length being such that when one end of it is heated steadily, the other end will be practically at the room temperature. Forbes used a bar of wrought iron 8 ft. long and $1\frac{1}{4}$ inch square section. One end of the bar is heated by immersing it in a high constant temperature bath of molten lead or silver. In the laboratory experiment a steam chamber is used to heat the end. The bar is provided with a series of holes at regular intervals into which thermometers are inserted with a little mercury in the holes for good contact, in order to record the temperature at different points along the bar when the steady state is reached. A non-conducting screen S protects the thermometers from the direct heat of the bath.

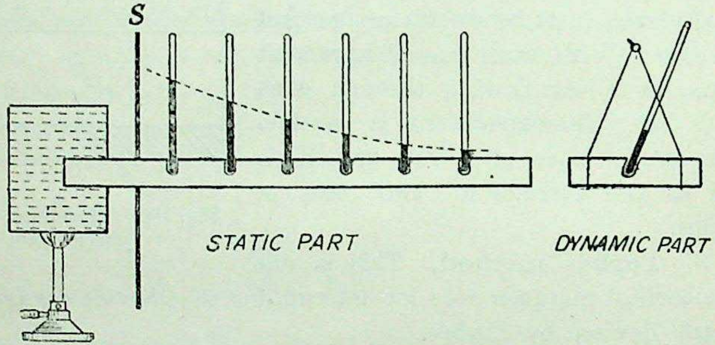


Fig. 106 Forbes apparatus.

Static experiment. After a long time of heating, the steady state is reached when the thermometers indicate constant readings. Forbes took nearly six hours to obtain the steady state. The temperatures indicated by the thermometers and their distances from the hot end are recorded. The temperature distribution is indicated by the dotted curve in Fig. 106 and obeys the relation $\theta = \theta_0 e^{-\mu x}$. A graph is plotted between the excess of temperature θ above that of the surrounding and the distance x from the hot end from the data obtained. A curve of the form shown in Fig. 107,

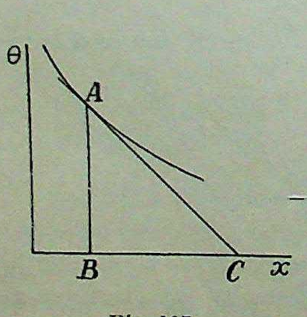


Fig. 107.

similar to the dotted curve mentioned above is obtained. This is known as the *static experiment*, since it deals with the steady state of heat flow. Drawing a tangent to the curve at a point corresponding to B near the hot end, the value of $\left(\frac{d\theta}{dx}\right)_B$ is obtained, since

$$\left(\frac{d\theta}{dx}\right)_B = \frac{AB}{BC}.$$

Dynamic experiment. A short piece of the original bar, or of a similar one with the same cross-section, is heated to a temperature attained by the hot end in the static experiment and then suspended in air to cool in exactly the same surroundings as the static bar. When the temperature of the bar reaches a value a little above than that of B chosen in the static part, readings of a thermometer inserted in a hole in the bar with a little mercury are taken at regular intervals of time and a cooling curve is plotted as shown in Fig. 108. This is known as the *dynamic experiment* since it deals with the variation of temperature with time.

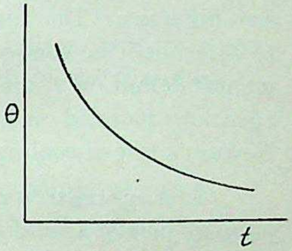


Fig .108.

Drawing tangents to this curve at points corresponding to the temperatures indicated by the thermometers in the different holes along the bar in the static experiment, the values of $\frac{d\theta}{dt}$ at the different distances x along the bar are obtained. With these data, a third graph is plotted with $\frac{d\theta}{dt}$ against x and a curve is obtained as shown in Fig. 109. The curve is prolonged to meet the x-axis. Then the area of the shaded portion, where B is the point chosen in the static experiment, is measured either by a planimeter or directly if the curve has been drawn on a graph paper, and gives the value of $\int_B^{end} \frac{d\theta}{dt}\,dx$.

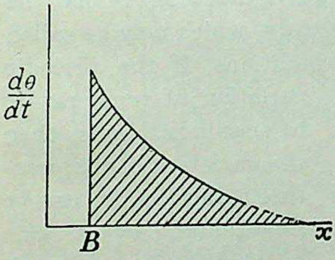


Fig. 109.

Hence K is obtained from

$$K = \frac{\rho s \times \text{area of shaded portion (Fig. 109)}}{AB/BC \text{ (Fig. 107)}}$$

It may be noted that different points can be taken as B and an average value of K can be found. The diffusivity $K/\rho s$ is also obtained in this experiment, for which it is not necessary to assume the values of ρ and s.

This method is not only tedious on account of the long hours required for the static part and of the data to be gathered for drawing the three graphs, but also fails to give accurate results, due to several sources of error, such as :—(*i*) the specific heat does not remain constant at different temperatures as assumed in the method, (*ii*) the distribution of temperature in the bar in the static and dynamic parts are different. The one great merit of the method is that it seeks to determine the conductivity absolutely, basing itself on the fundamental definition of the phenomenon, instead of using any theoretical equations founded on the hypotheses of constant conductivity and Newton's law of cooling.

4. **Angström's method.** Angström was the first to employ the *periodic flow of heat* along a bar to determine the conductivity of metals.

The *principle* of the method may be stated as follows. If a metallic bar is periodically heated and cooled at one end, the temperature at any point in the bar will also vary periodically. The bar will never reach a steady state, but if the alternate heating and cooling is continued for a sufficient number of times, the variation of temperature at any point will attain a fixed character so that the mean temperature at each point remains steady, which may be called the *steady periodic state*. Under these conditions, if the periodic variation of temperature be simple harmonic, then the variation of temperature along the bar can be represented by a sine curve of the damped type, as shown in Fig. 110, where the amplitude of the temperature variation diminishes as the distance from the hot end increases. It can be analytically expressed as $\theta = a \sin(\omega t + \beta)$ where

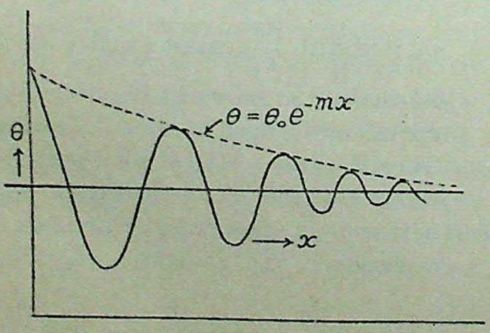


Fig. 110.

θ is the temperature of any point measured from the mean value at that point and t the time and a the amplitude $= \theta_0 e^{-mx}$ represented by the dotted curve.

The fundamental equation to be used in solving the problem of such a periodic flow of heat is

$$\frac{d^2\theta}{dx^2} = \frac{\rho s}{\mathrm{K}} \cdot \frac{d\theta}{dt} + \frac{\mathrm{E}p}{\mathrm{KA}} \cdot \theta \qquad \dots (1)$$

which we have already derived (*Cf.* p. 241). We have to solve this equation such that the *solution is a periodic function of time.*

Two cases can be considered :—

(*a*) *When the bar is covered* by a guard ring so that it is prevented from losing heat by radiation. Then equation (1) reduces to

$$\frac{d^2\theta}{dx^2} = \frac{\rho s}{\mathrm{K}} \cdot \frac{d\theta}{dt} \qquad \dots (2)$$

since the second term referring to heat spent in radiation is zero.

A simple harmonic solution of equation (2) which can be applied to the case is

$$\theta = ae^{-\alpha x} \sin (\omega t + \beta x + \gamma) \qquad \dots (3)$$

(*b*) *When the bar is naked, i.e.*, exposed to radiation, we have to use equation (1). Since the variation of temperature in this case is not simple harmonic but only periodic, the solution will be much more complicated, of the form :

$$\theta = a_0 e^{-\alpha_0 x} + a_1 e^{-\alpha_1 x} \sin (\omega t + \beta_1 x + \gamma_1) +$$
$$a_2 e^{-\alpha_2 x} \sin (\omega t + \beta_2 x + \gamma_2) + \cdots \qquad \dots (4)$$

This is the case which refers to Angström's experiment where the bar, which is periodically heated and cooled, is exposed to radiation.

The mathematical analysis of equation (3) is complicated and that of equation (4) much more so. But for the purpose of the experiment, we can arrive at a solution, considering the first two terms only of equation (4).

The temperature variation at a point distant x from the end which is periodically heated and cooled can be represented by

$$\theta_x = a_0 e^{-\alpha_0 x} + a_1 e^{-\alpha_1 x} \sin (\omega t + \beta_1 x + \gamma_1)$$

Putting $\mathrm{A}_0 = a_0 e^{-\alpha_0 x}$, $\mathrm{A}_1 = a_1 e^{-\alpha_1 x}$ and $\delta_1 = (\beta_1 x + \gamma_1)$, we have

$$\theta_x = \mathrm{A}_0 + \mathrm{A}_1 \sin (\omega t + \delta_1) \qquad \dots (5)$$
$$= \mathrm{A}_0 + \mathrm{A}_1 \sin \omega t \cos \delta_1 + \mathrm{A}_1 \cos \omega t \sin \delta_1$$

$$= A_0 + A_1 \sin \frac{2\pi t}{T} \cos \delta_1 + A_1 \cos \frac{2\pi t}{T} \sin \delta_1$$

where T is the period of the alternate heating and cooling of the bar.

Experimentally measuring θ_x at the four intervals, 0, T/4, T/2, 3T/4, we get

$$(t = 0) \qquad \theta^1{}_x = A_0 + A_1 \sin \delta_1 \qquad \ldots (6)$$

$$(t = T/4) \qquad \theta^2{}_x = A_0 + A_1 \cos \delta_1 \qquad \ldots (7)$$

$$(t = T/2) \qquad \theta^3{}_x = A_0 - A_1 \sin \delta_1 \qquad \ldots (8)$$

$$(t = 3T/4) \qquad \theta^4{}_x = A_0 - A_1 \cos \delta_1 \qquad \ldots (9)$$

From (6) and (8) we get $A_1 \sin \delta_1 = \dfrac{\theta^1{}_x - \theta^3{}_x}{2}$

From (7) and (9) we get $A_1 \cos \delta_1 = \dfrac{\theta^2{}_x - \theta^4{}_x}{2}$

Hence the value of A_1 and δ_1 can be found.

Making similar observations at another point x', the values of A_1' and δ_1' can also be found. The temperature variation at this point is represented by

$$\theta_x' = A_0' + A_1' \sin (\omega t + \delta_1') \qquad \ldots (10)$$

where $A'_0 = a_0 e^{-a_0 x'}$, $A_1' = a_1 e^{-a_1 x'}$ and $\delta_1' = (\beta_1 x' + \gamma_1)$.

Since $\quad A_1 = a_1 e^{-a_1 x}$ and $A_1' = a_1 e^{-a_1 x'}$

$$\frac{A_1}{A_1'} = e^{-a_1(x - x')} = e^{-a_1 l}$$

where $l = x - x'$, the distance between the two points.

$$\therefore \qquad \log \left(\frac{A_1}{A_1'}\right) = -a_1 l$$

$$\text{Or} \qquad a_1 = -\frac{1}{l} \log \left(\frac{A_1}{A_1'}\right) \qquad \ldots (11)$$

$$\text{Since} \qquad \delta_1 = \beta_1 x + \gamma_1 \text{ and } \delta_1' = \beta_1 x' + \gamma_1$$

$$(\delta_1 - \delta_1') = \beta_1 (x - x') = \beta_1 l$$

$$\therefore \qquad \beta_1 = \frac{\delta_1 - \delta_1'}{l} \qquad \ldots (12)$$

Mathematical analysis of equation (4) shows that the thermal diffusivity $\left(\dfrac{K}{\rho s}\right)$ is given by the expression

$$\frac{K}{\rho s} = -\frac{\omega}{2a_1\beta_1} \text{ where } \omega = \frac{2\pi}{T}$$

Substituting the values of a_1 and β_1 from (11) and (12)

$$\frac{K}{\rho s} = \frac{-2\pi/T}{2\left\{-\frac{1}{l}\log\left(\frac{A_1}{A_1'}\right)\right\}\left(\frac{\delta_1-\delta_1'}{l}\right)}$$

$$= \frac{\pi l^2}{T\log\left(\frac{A_1}{A_1'}\right)(\delta_1-\delta_1')}$$

$$\therefore \qquad K = \frac{\pi\, l^2\, \rho\, s}{T(\delta_1-\delta_1')\,\log\left(\frac{A_1}{A_1'}\right)} \qquad \ldots (13)$$

The *experiment* is conducted as follows. A long metallic bar is provided with a jacket at one end for alternate circulation of steam and cold water. Two thermometers are inserted in two holes drilled in the bar at a known distance l apart, with a little mercury for good contact. Steam is passed in the jacket for 10 mins., and water for 10 mins., so that the periodic time is 20 mins. or 1,200 secs. The two thermometers are read at 0, 5, 10, 15 mins. and the readings are recorded. After about half a dozen cycles of heating and cooling, the thermometer readings begin to have practically constant values at each of the four intervals, thereby indicating that the steady periodic state has been reached. The readings of the thermometers in the last cycle are utilised for calculation. From the two sets of the four readings A_1', and A_1', δ_1 and δ_1' can be estimated. Then, using the relation (13) and assuming the density ρ and the specific heat s of the material of the bar, the value of K can be calculated. To obtain accurate results a more complicated graphical method is employed, the details of which are beyond the scope of the book.

5. **Thermal conductivity of bad conductors.** All non-metallic bodies such as wood, cork, asbestos, rubber, glass, clay, etc., are poor conductors of heat. In measuring their conductivity, long bars or rods should not be used as in the case of metals, for it will be impossible to measure accurately the small rate of flow of heat even with a reasonably high temperature difference between the ends. Furthermore, since the rate of flow of heat by conduction Q is directly proportional to the cross-sectional area A and inversely proportional to the thickness d, it is advantageous to use the substance in the form of a thin plate, sphere or cylinder, of large area, so that Q becomes conveniently measurable, in spite of K being small. Of the various methods employed by different workers, we shall here describe the

following as typical :—(*i*) Lees' disc method, (*ii*) Nusselt's spherical-shell method and (*iii*) cylindrical tube method.

Lees' disc method. In the *original experiment*, the apparatus used was as shown in Fig. 111. The substance under test is taken in the form of two thin discs D_1 and D_2, about 2 mm. thick and 10 cm. in diameter. Each of them is pressed between two copper discs, D_1 between C_1 and C_2 and D_2 between C_3 and C_4. To ensure good thermal contact between the two copper discs and the experimental disc, a thin layer of glycerine is applied to the surfaces in contact. The purpose of sandwiching the experimental disc between two copper discs is to secure the flow of heat normal to the faces in the disc, which being a bad conductor can support an irregular distribution of heat without a big flow of heat in the direction normal to the faces. Copper being a good conductor helps to have the flow normal. The copper discs also serve to measure conveniently the temperature of the faces of the experimental disc. A heater coil H is arranged at the centre, between the copper discs C_1 and C_3, as in the figure. Thermocouples T_1, T_2, T_3 and T_4 are used to measure the temperatures of the two faces of each of the discs D_1 and D_2, one junction of each thermocouple being inserted in a small hole drilled in the edge of the respective copper disc. The whole apparatus is kept suspended in a constant temperature enclosure.

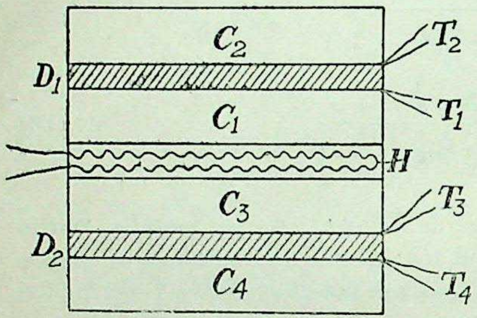


Fig. 111. Lees' disc method.

A current of I amperes at a P.D. of E volts is passed through the heater coil. When the steady state is reached, the constant temperatures θ_1, θ_2, θ_3 and θ_4 as indicated by the respective thermocouples are noted. The quantity of heat supplied by the heater coil per second is equal to the quantity of heat passing through D_1 and D_2 in the same time, and in the steady state this amount of heat is radiated away almost from the surfaces of the copper discs C_2 and C_4, since radiation from the edges of C_1, C_3, D_1 and D_2 is negligible. It does not matter how the radiation takes place, since the heat lost by radiation is not measured for finding K in this method.

Using the general relation $Q = KA\dfrac{\theta_1 - \theta_2}{d}$,

heat conducted per second through $D_1 = \dfrac{KA(\theta_1 - \theta_2)}{x_1}$

heat conducted per second through $D_2 = \dfrac{KA(\theta_3 - \theta_4)}{x_2}$,

where x_1 and x_2 are the thicknesses of D_1 and D_2 and A the area of each of the discs D_1 and D_2.

As EI/J is the quantity of heat supplied by H per second,

$$\frac{EI}{J} = KA\left\{\frac{(\theta_1 - \theta_2)}{x_1} + \frac{(\theta_3 - \theta_4)}{x_2}\right\}$$

In this relation assuming the value of J, all the quantities except K are measured experimentally ; K therefore can be calculated.

Lees and Charlton have proposed another design of the apparatus, which is ordinarily used in the *laboratory experiment*. A flat, circular, hollow metal box A, which serves as a steam chamber, is suspended from a retort stand so that its top face is horizontal (Fig. 112). A thin disc D of the material under test, such as wood, ebonite, cardboard, etc., is placed. on the top of A and over it a thick nickel-polished cylindrical brass slab B, so that D is well pressed between A and B, both of these being provided with thermometers T_1 and T_2 to record the temperatures of steam and of the slab respectively during the experiment.

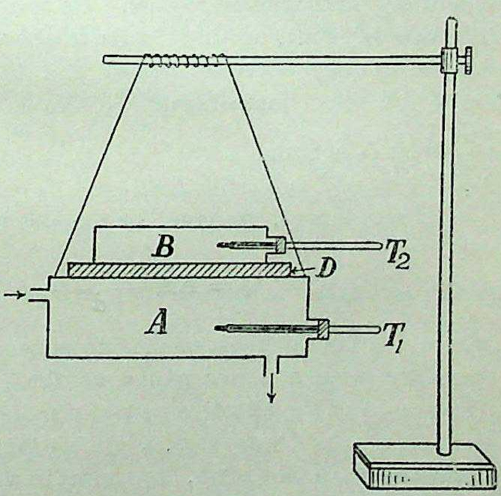


Fig. 112. Less and Charlton apparatus.

Steam is passed through A for a pretty long time until the steady state is reached, *i.e.*, until T_1 and T_2 (chiefly the latter) give constant readings. The thermometers are then read, which give the temperatures θ_1 and θ_2 of the hot and cold faces respectively of the experimental disc D. In the steady state, the rate of flow of heat Q is equal to the rate at which heat is radiated from the side and top surface of the slab B. Hence if the rate of radiation $(d\theta/dt)$ from B at θ_2 is measured, knowing the mass m of B and its specific heat s, Q can be found.

$$Q = m.\ s.\ \frac{d\theta}{dt} \cdot \left(\frac{r + 2l}{2r + 2l}\right) \qquad \dots (1)$$

where r is the radius of the slab and l its thickness. The quantity within the bracket gives that fraction of the total radiation which refers to the side and top surface of the slab.

To measure $\frac{d\theta}{dt}$, the experimental disc is removed, the slab B is placed directly on the steam chamber A and heated till its temperature rises to about 10°C above θ_2. The slab is then suspended separately and allowed to cool. Its temperature is noted at regular intervals of time, until it falls to about 10°C below θ_2. With the data a cooling curve is drawn and from the tangent to the curve at the temperature θ_2, the rate of fall of temperature $\left(\frac{d\theta}{dt}\right)$ at θ_2 is found.

From theory, we have, for the steady state,

$$Q = KA\,\frac{\theta_1 - \theta_2}{d} \qquad \dots (2)$$

where d is the thickness of the experimental disc, which is measured carefully with a screw gauge as the average of several readings. The area A of the effective part of the disc is given by πr^2 where r is the radius of the brass slab, assuming the disc to be slightly of larger diameter than the slab, as shown in the figure. From (1) and (2), we have

$$ms\,\frac{d\theta}{dt}\left(\frac{r + 2}{2r + 2l}\right) = K\pi r^2\,\frac{\theta_1 - \theta_2}{d}.$$

Hence K can be found.

Nusselt's spherical shell method is well suited for substances which are available in powder form, such as sand, asbestos, clay, cork, charcoal, etc. The apparatus, shown in Fig. 113, consists of a hollow copper sphere C, of about 1 ft. in diameter, inside which another concentric hollow aluminium sphere A, about ½ ft. in diameter, is arranged. The spheres are split into two halves, so that they can be separated into two pieces each or put together. The space between the spheres is well packed with the substance B under test in powdered form. A spherical electric heater H is placed at the centre of the spheres and electrical energy is supplied at a known constant rate. Temperatures at different points in the material B along one or more radii are measured by means of thermocouples inserted at those points. Using the relation appropriate to the case *viz.*

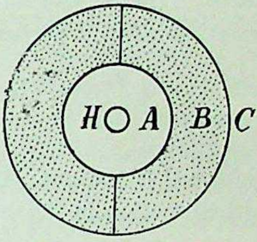


Fig. 113. Nusselt's apparatus.

$$Q = \frac{EI}{J} = \frac{4\pi K(\theta_1 - \theta_2) r_1 r_2}{r_2 - r_1} \quad (\textit{Cf.}\ \text{p. } 243)$$

where I is the current in amps. passing through the heater under a p.d. of E volts, J is the mechanical equivalent of heat, θ_1 and θ_2 are the temperatures of points distant r_1 and r_2 from the centre, the conductivity Q can be found.

Cylindrical tube method. As the experiments ordinarily performed in the laboratory to determine the conductivity of rubber and glass given in the form of tubes are typical of this method, we shall describe them.

Conductivity of rubber. A known length *l* of a rubber tubing is immersed in a weighed amount of water contained in a calorimeter C (Fig. 114). Steam is passed through one end of the rubber tube and let off through the other. The contents of the calorimeter are stirred with a stirrer S and the rise in temperature is noted with a sensitive thermometer T. The inner surface of the tube will soon attain the temperature of steam, so that heat will flow through the wall of the tube to the outer surface in contact with the water in the calorimeter. Steam is cut off when the temperature has risen by about 10°C. The time *t* for which steam is passed is noted. The initial and final temperatures θ_1 and θ_2 of calorimeter and contents are also noted. The final temperature is cor-

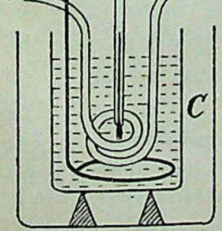


Fig. ,114. Conductivity of rubber.

rected for loss of heat by radiation using, say, Barton's method. The internal and external radii r_1 and r_2 of the rubber tube are measured by taking ink-prints of the cross-section of the tube. With these data, K, the conductivity of rubber, can be obtained using the relation already derived (*Cf.* p. 244) *viz.*

$$K = \frac{Q \,.\, \log_e (r_2/r_1)}{2\pi l\left(\theta_3 - \dfrac{\theta_1 + \theta_2}{2}\right)}$$

where Q is the quantity of heat flowing per second across any cylindrical section in the wall of the tube, which is got from

$$Q = \frac{(m + w)\,(\theta_2 - \theta_1)}{t}$$

(m = mass of water taken in the calorimeter, w = water equivalent of calorimeter and contents, θ_1 initial temperature of water, θ_2 final temperature corrected for radiation) ;

θ_3, the temperature of steam, gives the temperature of the hot side of the tube,

and $\dfrac{\theta_1 + \theta_2}{2}$ gives the temperature of the cold side of the tube.

In this method Q is measured by the use of a calorimeter.

Conductivity of glass. A glass tube A is enclosed in a bigger tube C which serves as a steam jacket (Fig. 115). Two T-pieces are connected to the ends of A, with provisions for inserting two thermometers T_1 and T_2 and for making a steady stream of water flow through the tube. A spiral wire is placed inside A in order that the water may be in good contact with the inner surface of A all along its length. The whole apparatus is arranged in a slightly slanting position, so that the flow of water may be from a lower to a higher level, which helps for good contact of water with the wall of the tube.

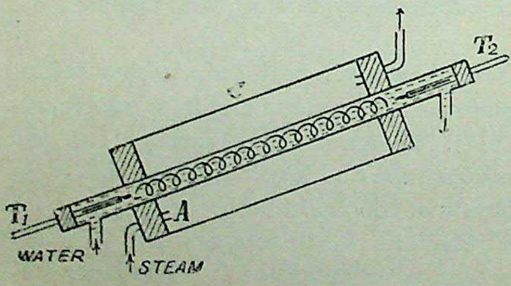


Fig. 115. Conductivity of glass.

Steam is passed through C and the flow of water through A is adjusted so that there is a decent difference of temperature in the water at entry and at exit. Soon the outer surface of A will acquire the temperature of steam and heat will flow through the wall of A. When the steady state is reached, as indicated by the steady readings of the thermometers T_1 and T_2 which measure the temperatures of the inflowing and outflowing water respectively, these temperatures θ_1 and θ_2 are noted. Then the outflowing water is collected in a weighed beaker for a known time t and the mass m of water thus collected is found. The length l of the tube A exposed to steam, hence the distance between the inner surfaces of the two corks closing the steam jacket is measured. The internal and external radii r_1 and r_2 of the tube are measured with a calipers or using a travelling microscope.

With these data, the conductivity K of the material of the glass tube can be found using the relation

$$K = \frac{Q \cdot \log_e (r_2/r_1)}{2\pi l \left(\theta_3 - \dfrac{\theta_1 + \theta_2}{2}\right)}$$

where Q, the quantity of heat flowing per second across any cylindrical section in the wall of the tube, is given by

$$Q = \frac{m(\theta_2 - \theta_1)}{t}$$

θ_3 is the temperature of steam, *i.e.*, of the hot side of the tube, and $\dfrac{\theta_1 + \theta_2}{2}$ the average temperature of water flowing through the tube, which is taken as the temperature of the cold side of the tube.

In this method Q is measured by using a constant flow calorimeter.

6. **Conductivity of crystals.** For isotropic bodies, which we have considered above, the conductivity is the same in all directions, but for anisotropic and crystalline bodies the conductivity is different in different directions. De Senarmont was the first to make systematic investigations on the conductivity of crystals. The simple method used by him is as follows. A thin plate with parallel faces is cut from a crystal in any desired direction, and the two faces are coated with a thin layer of wax. Heat is applied at one point in the plate either by passing an electrically heated wire through the point or by focusing the sun's rays on the point. The wax round the point melts and in the final steady state the boundary line of the melted wax represents an isothermal line corresponding to the melting point

of wax ; the shape of the boundary clearly indicates the inequalities of conductivity in different directions. The conductivities in the various directions can be compared from the lengths up to which wax has melted in those directions, as in the Ingen-Hausz's experiment. The following interesting results were obtained by De Senarmont. Substances such as glass and cubic crystals exhibit a circle for the isothermal boundary line, while other crystals, in general, form ellipses. The isothermal surfaces round the heated point are a system of concentric ellipsoids, the axes of which are called the *thermic axes* of the crystal and coincide with the *crystallographic axes* of symmetry. For any crystal, the isothermal curves are found to be circles in plates cut perpendicular to the axis and ellipses in plates cut parallel to the axis.

Eucken, using a modification of Lees' disc method, measured the absolute conductivity of crystals over a wide range of temperature up to − 252°C and discovered that the conductivity of crystals varied inversely as the absolute temperature. This is only an empirical law ; no satisfactory explanation has yet been given.

CONDUCTIVITY OF LIQUIDS

In the determination of the conductivity of liquids, one is faced at the very outset with the problem of eliminating convection which will transmit much more heat than conduction. This has been very satisfactorily solved by heating the liquid at the top when no convection can occur.

The methods that have been employed for the measurement of the conductivity of liquids are the following :—

1. **Column method.** Despretz was the first to employ this method. The liquid is taken in a tall jar and is heated at the top by passing hot water in a copper vessel, maintained at a constant temperature. When the steady state is reached, the temperatures at various depths are noted with thermometers inserted at those points. It is found that the law governing the rectilinear flow of heat along a bar holds good in the present case also. Using different liquids and noting the depths at which the liquids have the same temperature, their conductivities can be compared as in Ingen-Hausz's experiment.

Berget used this method to determine the absolute conductivity of mercury with an additional safeguard of surrounding the vertical column of mercury with an annular ring of mercury. The upper surfaces of both are heated by steam, while the lower surfaces rest on a metal plate cooled by ice, so that the temperature gradient and the temperature at the same level in the two liquid columns, *viz.*, experimental and guard ring, are identical. The lower end of the experimental column projects into a Bunsen ice calorimeter, by means of which the heat flowing at the lower cold end can be measured. The temperature gradient is determined by measuring the temperatures at several depths in the column in the steady state, using differential thermocouples. With these data, the conductivity K of mercury is calculated using the relation :

$$Q = KA \frac{\theta_1 - \theta_2}{d} t.$$

Weber extended this method to the determination of conductivity of other liquids, with the following modifications : (*i*) The liquid column and the guard ring are heated at the top by an electrically heated oil bath. (*ii*) The bottom of the column is cooled by copper plate placed on ice and the heat conducted away is found from the amount of ice melted.

2. **Hot-wire or cylindrical tube method.** Goldsmith employed this method, the theory of which is the same as that of the cylindrical tube method of determining K of solids. The liquid is contained in a silver capillary tube of 2 mm. in diameter and heated by passing electric current through a wire stretched along the axis of the tube. The temperature of the wire is known from its resistance and the amount of heat flowing across any isothermal cylindrical surface of the liquid in the steady state is found from the rate of electrical energy supplied to the wire. Ths conductivity K of the liquid is calculated using the relation

$$K = \frac{Q \,.\, \log (r_2/r_1)}{2\pi l\,(\theta_1 - \theta_2)}$$

where r_1 and r_2 are the radii of the wire and the capillary tube respectively.

3. **Film or Lees' disc method,** employed by Lees, Milner and Chattock and others, is probably the most accurate so far devised for determining the conductivity of liquids. The *principle* of the method is to force heat first through a disc of a solid bad cnnductor of known conductivity and then through a *disc* or *film* of the liquid under test. If the area and the temperature gradient of each disc are known, the rate of flow of heat through the liquid film can be calculated from the known conductivity of the solid and used to find the conductivity of the liquid.

Lees' apparatus, used for this purpose, is shown in Fig. 116. The liquid under test L is enclosed in an ebonite ring E arranged between two copper discs D_1 and D_2. A glass disc G of known conductivity is placed above D_2 and above G is another copper disc D_3. Above D_3 is an electric heater coil H which is held in position by another copper disc D_4. The pile thus built up is varnished to give it a uniform and known emissivity and mounted horizontally in a constant temperature enclosure of air. Thermocouples are inserted as shown in the figure to measure the temperatures of the faces of G and L.

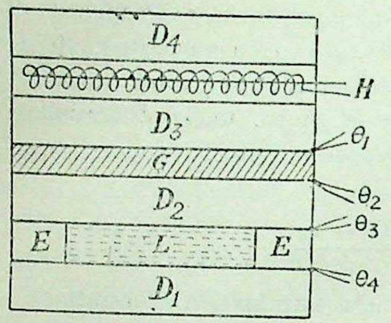


Fig. 116. Lees' apparatus for conductivity of liquids.

The current is switched on in the heater coil and when the steady state is reached the readings of the four thermocouple thermometers are noted, from which θ_1 and θ_2 the temperatures of the two faces of G and θ_3 and θ_4 those of the two faces of L are found. Let K, A and d be the conductivity, cross-sectional area and thickness respectively of the liquid, K_1, A_1 and d_1 similar quantities of the glass disc and K_2, A_2 and d_2 for the ebonite ring.

The heat flowing across any plane in G per second

$$= K_1 A_1 \frac{\theta_1 - \theta_2}{d_1}$$

This is equal to the sum of the heat flowing across any plane in the liquid film and the ebonite ring per second, which is given by

$$KA \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2}$$

$$\therefore \qquad K_1 A_1 \frac{\theta_1 - \theta_2}{d_1} = KA \frac{\theta_3 - \theta_4}{d} + K_2 A_2 \frac{\theta_3 - \theta_4}{d_2}$$

from which K, the conductivity of the liquid, can be obtained. A small correction has to be applied for the heat radiated from the curved sides of the discs G, D_2 and E, which has not been taken into account in the above relation.

CONDUCTIVITY OF GASES

The determination of the conductivity of gases is beset with still greater difficulties, because the very small conduction to be measured is masked by the accompanying large convection and radiation effects. Furthermore, as it is necessary to use some solid vessel to contain the gas, the heat conducted through the vessel is bound to be much greater than that which is transmitted through the gas. Many methods have been devised to overcome these difficulties. We shall describe here only the following two, which have met with a good measure of success.

1. **Hot-wire method**, first suggested by Andrews and actually employed by Schleiermacher for determining the absolute conductivity of a gas, works on the same principle as the analogous methods for liquids. An electrically heated wire is surrounded by a coaxial cylindrical tube filled with the gas under study. The temperature of the wire is known from its resistance. The amount of heat flowing across the curved surface of the cylindrical column of the gas is found from the rate of energy supplied to the wire. The conductivity is calculated from the relation appropriate to the case (*Cf*. p. 263). In this arrangement convection effect is very much reduced as there is no temperature gradient in the vertical direction. What is left over is eliminated by using the results obtained by Kundt and Warburg who have shown that when the pressure of the gas is kept under 150 mm., convection effect becomes negligible. Radiation loss is corrected for by repeating the experiment with the tube completely evacuated when conduction effect becomes negligible. Correction is applied also for loss of heat by conduction along the leads supplying the current to the wire.

Weber improved the apparatus and dealt with the various corrections more thoroughly. The end-effect was determined by varying the length of the tube. Convection effects were studied by working with the tube both in the horizontal and vertical positions.

Gregory and Archer (Proc. Roy. Sec. 110, 91, 1926) further improved the experimental technique and studied the corrections to be applied quantitatively. They investigated the losses due to convection in the gas and conduction along the wire itself. Further, the non-uniformity of temperature along the wire was also corrected for. On account of these factors, the equation of heat transmission used by them is rather complicated.

2. **Film method,** originally used by Todd, has been employed more recently by Laby and Hercus with improved technique which has given the best results. The *basic principle* of their method is the

same as in Lees' similar experiment devised for liquids (*Cf.* p. 264), *viz.*, to supply heat electrically to the top of a horizontal disc or film of the gas thereby eliminating convection and remove the heat at a constant rate from the bottom layer by water cooling, so that a uniform temperature gradient is established. But, in order to prevent any escape of heat from the curved surface of the disc of gas, they used the ingenious device of a "guard-ring" of the same gas with the same temperature gradient as the experimental gas. This guard-ring had a further advantage of ensuring the lines of heat flow to be parallel to the axis to the disc of gas all over its surface.

The *apparatus* used by Laby and Hercus is shown in Fig. 117. The gas under test is contained between two copper plates A and B, whose surface are accurately planed flat and silvered so as to reduce radiation to a minimum. The plate A is cooled by a stream of water passing over its lower surface. The plate B is made up of two sheets of copper between which a heater coil, well-insulated, is placed. To prevent loss of heat by radiation from the top face of B another copper plate C also planed and silvered is mounted above B and kept at the same temperature as B by another heater coil. In order that the heat applied to B may not flow down the walls of the containing vessel and also that the lines of flow of heat may be everywhere normal to the face of B, a metal guard-ring G surrounds B and is maintained at the same temperature as B by a third heater coil. The temperatures of A, B, C and G are measured by thermocouples, which are formed by attaching constantan wires to the respective plates, so that the plates themselves act as one metal of the couple. The plate B is attached to the guard-ring by ivory buttons and the plates A, G and C are clamped together by screws and glass distance-pieces. The

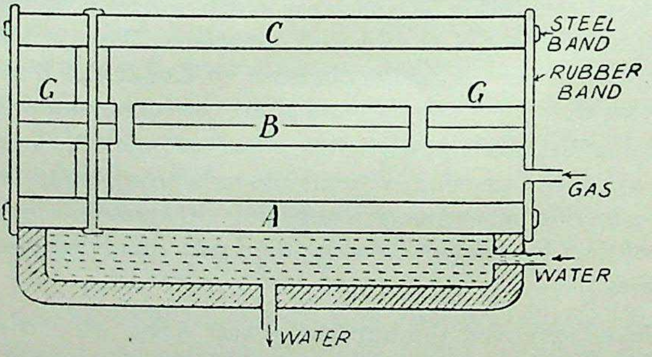


Fig. 117. Apparatus of Laby and Hercus.

apparatus is made gas tight by a stout rubber collar clamped to A and C by steel bands.

In performing the experiment, the heating currents in B, C and G are switched on. While B and G are kept at the same temperature, C is maintained at a temperature little above, in order to eliminate any possible convection effect. This, however, introduces a small correction due to radiation. When the steady state is reached, the temperatures of A and B are measured by the thermocouples attached to them. The conductivity K of the gas is calculated using the relation

$$\frac{\mathrm{EI}}{\mathrm{J}} = \mathrm{K\,A}\frac{\theta_1 - \theta_2}{d}$$

where E and I are the P.D. and current through the heater coil in B, A the mean of the areas of cross-section of B and the gap between B and G, θ_1 and θ_2 the steady temperatures of A and B and d their distance apart. The heat transmitted from C to B and from B to A by *radiation* must be subtracted from EI/J. The radiation correction is determined by a separate experiment on a silvered Dewar flask and is found to amount to about 2% only of the total quantity.

Results. The values of the conductivity of a few substances, solids, liquids and gases, are given in the following table in calorie per sec., per sq. cm. per unit temperature gradient.

Substance	*K*	*Substance*	*K*
Silver	1·01	Mercury	0·020
Copper	0·92	Water	$14{\cdot}1 \times 10^{-4}$
Zinc	0·265	Glycerine	$6{\cdot}8 \times 10^{-4}$
Cast iron	0·114	Alcohol	$4{\cdot}3 \times 10^{-4}$
Lead	0·085	Turpentine	$3{\cdot}25 \times 10^{-4}$
Crown glass	$2{\cdot}5 \times 10^{-3}$	Hydrogen	$31{\cdot}8 \times 10^{-5}$
Mica	$1{\cdot}8 \times 10^{-3}$	Oxygen	$5{\cdot}83 \times 10^{-5}$
Asbestos	$0{\cdot}6 \times 10^{-3}$	Air	$5{\cdot}40 \times 10^{-5}$
Rubber	$0{\cdot}45 \times 10^{-3}$	Argon	$3{\cdot}89 \times 10^{-5}$
Ebonite	$0{\cdot}42 \times 10^{-3}$	Carbon dioxide	$3{\cdot}43 \times 10^{-5}$

It is seen that silver is the best conductor of heat ; mercury, though placed among liquids, should be classified with metals on account of its comparatively high value. Liquids have a low conductivity, but gases extremely low, of the order of 10^{-5}. Hydrogen appears to be the best conductor among gases ; but helium has a slightly higher value ($33{\cdot}9 \times 10^{-5}$).

Relation between thermal and electrical conductivities of metals.—Wiedemann-Franz law. The above table shows that all good conductors of electricity are also good conductors of heat. The close connection between electrical and thermal conductivities has long been known. As early as 1853, Wiedemann and Franz had discovered that *the ratio of the thermal to the electrical conductivities at any particular temperature is the same for all metals.* Lorentz later showed that *the ratio is proportional to the absolute temperature.* Hence $K/\sigma T$ = constant, where K is the thermal conductivity, σ the electrical conductivity and T the absolute temperature. This is generally known as the *Wiedemann-Franz Law.* This conclusion has been put to experimental test by Jaeger and Diesselhorst and by Lees. The following table gives Lees' results.

Metals	Values of $\frac{K}{\sigma T} \times 10^8$				
	− 170°C	*− 100°C*	*− 50°C*	*0°*	*18°C*
Aluminium	1·50	1·81	1·98	2·09	2·13
Copper	2·85	2·17	2·26	2·30	2·32
Silver	2·04	2·29	2·36	2·33	2·33
Zinc	2·20	2·39	2·40	2·45	2·43
Lead	2·55	2·54	2·52	2·53	2·51
Iron	3·10	2·98	2·93	2·97	2·99
Brass	2·78	2·54	—	2·45	2·45

It is seen that the law fits experimental data pretty well at ordinary temperatures, but deviations occur at low temperatures, the value decreasing as the temperature becomes low. At low temperatures both the electrical and thermal conductivities are found to increase, but the former much more rapidly, tending to become infinite at the absolute zero, except for the existence of the phenomenon of superconductivity.

Drude explained the relation between the thermal and electrical conductivities of metals on the basis that these processes take place through the same intermediary *viz.*, *free electrons*, which were assumed to exist in metals. He was even able to derive a theoretical expression for $K/\sigma T$, which was confirmed fairly well by the experiments of Jaeger and Diesselhorst. This electron theory was later substantially modified by the application of the quantum theory in order to account for other experimental facts, such as, for instance, the specific heat of both metals and non-metals being nearly the same.

Practical applications of heat conduction. 1. Conductivity of the earth's crest. The method of determining conductivities by periodic heating and cooling has been applied to estimate the conductivity of the earth's crest. For, by day the surface of the earth is heated and by night it is cooled. This alternate heating and cooling travels into the interior of the earth in the form of a heat wave (*diurnal wave*) and gives rise to diurnal variations of temperature at points inside the earth's crest. There is also a similar periodic heating and cooling during summer and winter, which gives rise to the *annual wave* travelling into the interior of the earth.

Assuming that these waves are simple harmonic to a first approximation, the phenomenon can be assimilated to the case of the periodic flow of heat along a *covered* bar so that the differential equation to be used is :

$$\frac{d^2\theta}{dx} = \frac{\rho s}{\mathrm{K}} \cdot \frac{d\theta}{dt}$$

with its simple harmonic solution

$$\theta = a\, e^{-ax} \sin(\omega t + \beta x + \gamma)$$

(*Cf.* p. 253). Analysing this solution it can be shown that the thermal diffusivity h ($= \mathrm{K}/\rho s$) is given by

$$h = \frac{\lambda^2}{4\pi \mathrm{T}} \qquad \ldots (1)$$

where λ is the wavelength of the temperature wave, and T the periodic time.

If a number of thermometers are embedded in the earth at different depths, the periodic variations of temperature can be investigated and thus knowing the wave length λ, the diffusivity h and consequently the conductivity K can be calculated using relation (1) and assuming T, ρ and s.

On the other hand, if the value of h for ordinary moist earth is assumed, the wave length λ can be estimated from the relation $\lambda = 2\sqrt{\pi h \mathrm{T}}$ deduced from (1) ; similarly the velocity of propagation v can also be found using $v = 2\sqrt{\pi h/\mathrm{T}}$ deduced again from (1) by putting $\lambda = v\mathrm{T}$. Calculations show that for the diurnal wave $\lambda = 73$ cm. and $v = 8{\cdot}4 \times 10^{-4}$ cm /sec. and for the annual wave $\lambda = 14$ metres and $v = 3{\cdot}9$ cm./day. Likewise, it is found that the diurnal wave will penetrate to a depth of about 1 metre, while the annual wave to about 19 metres. These theoretical predictions have been verified experimentally.

2. **Underground temperature—age of the earth.** If the mean temperatures at different depths in the interior of the earth are compared they are found to increase as we descend. Hence there must be a flow of heat from the interior to the surface. The amount of heat that escapes from the earth per annum can be estimated if the conductivity of the earth's crest is known. Having thus calculated the present rate of loss, one can work backwards to find what the temperature of the earth must have been in times past. In this manner Lord Kelvin has shown that it cannot be more than one or two hundred million years since the earth was a molten mass, on which a solid crest was just beginning to form.

3. **Davy safety lamp.** The good conductivity of metals and the bad conductivity of gases are made use of in the construction of the Davy safety lamp. The flame of the lamp is enclosed in an iron gauze chimney, so that when the lamp is taken in an explosive region in a coal mine, the combustible gases penetrate the gauze and burn coming into contact with the flame, but only *inside* the chimney, since the gauze conducts away heat so quickly that the temperature at any point in it does not reach the ignition point and the poorly conducting gas outside does not burn. As soon as the miner notices this phenomenon, he leaves the place of danger. It has been found, however, that such a device is not an efficient protection against all explosions.

4. **Other applications.** The conductivity of materials, such as glass-wool, brick walls, granite, etc., are of great importance in the construction of cold storage, furnace boiler, etc. Vacuum being a very bad conductor, is utilised in the construction of thermos flasks. Woollen clothes protect us from cold on account of the air enclosed in the fabric, air being a very poor conductor of heat.

CONVECTION

As a detailed study of the phenomenon of convection is beyond the scope of this book, we shall give here only some illustrative examples that occur in Nature and some practical applications in science and industry.

1. **Illustrative examples that occur in Nature. Winds** are due to convection currents set up in the atmosphere by unequal heating. For instance, *trade winds* are caused as follows. The earth in the tropics becomes greatly heated and this heat is communicated to the air, which in consequence becomes lighter and rises up.

To replace this air a current of cold air flows in from the polar and temperate regions, thus causing a northerly and southerly wind from the northern and southern hemispheres respectively. Owing to the rotation of the earth these winds appear to come from north-east and south-east directions and hence are called *north-east* and *south-east trade winds.*

Land and sea breezes arise in a similar manner. In sea coasts a breeze blows from sea to land during the day and from land to sea during night. Land, having a lower specific heat than water, gets warmed up more quickly than water in the sea by the sun's heat during the day. Consequently the air above the land gets heated and rises and the cooler air from the sea flows in to take its place, thus causing a *sea breeze.* After sunset, however, the land which has acquired less heat than the sea on account of its lower specific heat, cools more quickly than the sea and the air above it becomes cooler than that above the sea ; the direction of the current of air is then reversed and during the night a *land breeze* sets in.

2. **Applications in science.** (*a*) **Newton's law of cooling,** which states that *the rate of cooling is proportional to the excess temperature,* applies to cooling by *convection and radiation* and not by radiation alone. In practice, this condition is realised when the hot body is allowed to *cool in a good draught* to make the loss due to radiation small as compared to that due to forced convection. In the determination of the specific heat of a liquid by the method of cooling *through radiation alone,* we have already established the relation

$$m\,s\,d\theta = \mathrm{K}\,f\,(\theta)\,dt \qquad \dots (1)$$

where m is the mass of the liquid, s its specific heat, $d\theta$ the fall of temperature in time dt due to cooling, K a constant depending on the area and nature of the cooling surface and θ the excess of temperature (*Cf.* p. 130). Now, according to Newton's law, $f\,(\theta) = \theta$, so that equation (1) becomes $m\,s\,d\theta = \mathrm{K}\,\theta\,dt.$

Or $dt = -\dfrac{m\,s\,d\theta}{\mathrm{K}\theta}$, ($-$ *ve* sign is added, since $d\theta$ represents a fall in temperature). Integrating, we get

$$t = -\frac{ms}{\mathrm{K}}\log_e \theta + \mathrm{C}\ \text{(constant of integration)} \qquad \dots (2)$$

To determine C, applying initial conditions, *i.e.*, at $t = 0$, $\theta = \theta_0$, the initial temperature from which cooling starts,

$$\mathrm{C} = \frac{ms}{\mathrm{K}}\log_e \theta_0$$

$$\therefore \qquad t = -\frac{ms}{K}\log_e \frac{\theta}{\theta_0}$$

Or $$\theta = \theta_0 \, e^{-\frac{Kt}{ms}} \qquad \ldots (3)$$

The cooling curve is therefore an *exponential curve* in the region in which Newton's law holds good, *i.e.*, when the excess of temperature is not large. A graph between $\log_e (\theta - \theta_0)$ and time t will be a straight line. At higher temperature, the cooling is more rapid than that allowed by Newton's law and no simple relation holds.

To *verify Newton's law of cooling*, a calorimeter, with a large surface area, blackened on the outside and containing the hot liquid is allowed to cool in a steady draught. The temperature of the liquid at regular intervals of time, say every minute, is noted, while keeping the liquid constantly stirred. Plotting $\log_e (\theta - \theta_0)$ against t a straight line will be obtained proving the truth of Newton's law of cooling.

(*b*) **Convective equilibrium in the troposphere.** It is found that the temperature decreases continuously, as one goes up in the atmosphere. Up to about 15 to 16 km., there is a rapid fall of about 5°C per km. which is known as the *lapse rate*. But after that height the rate of fall diminishes and at a height of about 20 km., the temperature becomes almost constant. This has necessitated a division of the atmosphere into two regions, the lower one called the *troposphere* or *convective zone*, in which there is a considerable fall of temperature with height and the upper one called the *stratosphere* or the *advective zone*, in which the temperature does not change sensibly with height. The surface of separation between these two layers of the atmosphere is known as the *tropopause*, which varies with the latitude. As one proceeds from the equator to the poles, the tropopause gets lower, its height at the equator being about 14 km., while at the poles about 8 to 10 km.; the tropopause is higher in summer than in winter.

The fall of temperature with height in the troposphere is due to convection in that region. The earth's surface heated by sun's rays warms the air above it, partly by contact and partly by the long wavelength heat radiations emitted by it and absorbed by the air. Now the temperature of air at any height depends upon the total energy absorbed and emitted by it. The lower atmosphere emits more energy than it absorbs and hence tends to cool by radiation. The heating of the earth on the one hand and the cooling of the layer of air above on the other affect the density of the atmosphere in such a way as to cause vertical convection. The warm ascending air becomes cooled through adiabatic expansion and the descending air becomes heated through adiabatic compression, since the pressure of the atmosphere decreases with increase of altitude. By such a convective or adiabatic equilibrium, the decrease of temperature with increase in height is established and maintained in the lower region of the atmosphere, the troposphere.

Above the troposphere, convection becomes negligible, since the heat received by the air in that region from the earth remains practically constant, so that the temperature of the atmosphere falls so much that the heat radiated by it becomes equal to the amount absorbed by it and in consequence the temperature of the layer remains practically constant. The stratosphere therefore results from the cessation of convection currents and the establishment of radiative equilibrium.

The *lapse-rate in the troposphere* may be calculated as follows :—

Let $-dp$ be the decrease in pressure corresponding to an increase in height dh. Then, if ρ is the density of the air at the point considered

$$-dp = dh \cdot g \cdot \rho \qquad \dots (1)$$

On account of the convective equilibrium in the troposphere, the law connecting the pressure and volume of the air must be an *adiabatic law* to a first approximation, *viz.*,

$$pv^{\gamma} = \text{C (constant)} \quad \text{or} \quad p = \text{C}\,\rho^{\gamma} \qquad \dots (2)$$

Differentiating (2) with respect to height h

$$\frac{dp}{dh} = \text{C}\,\gamma\,\rho^{\gamma-1}\,\frac{d\rho}{dh}$$

Substituting for $\frac{dp}{dh}$ from (1), we get

$$\text{C}\,\gamma\,\rho^{\gamma-1}\,\frac{d\rho}{dh} = -\,g\rho \qquad \dots (3)$$

Integrating (3),

$$\frac{\text{C}\,\gamma}{\gamma-1}\,(\rho_0{}^{\gamma-1} - \rho^{\gamma-1}) = gh \qquad \dots (4)$$

where ρ_0 is the density at zero height.

Relation (4) represents the manner in which the density of air falls with increase in height in the troposphere.

Assuming that the ideal gas laws apply to the air in the troposphere, we have $p = \rho RT/M$, where M is the molecular weight.

Hence equation (2) can be written as

$$\frac{\rho RT}{M} = C\,\rho^{\gamma}$$

Or $$\rho^{\gamma-1} = \frac{R}{CM}\cdot T$$

Substituting this in (4),

$$\frac{C\gamma}{\gamma-1}\left(\frac{R}{CM}\cdot T_0 - \frac{R}{CM}\cdot T\right) = gh$$

Or $$\frac{\gamma}{\gamma-1}\cdot\frac{R\,(T_0 - T)}{M} = gh$$

where T_0 is the temperature at zero height.

Since $\gamma = C_p/C_v$ and $JM(C_p - C_v) = R$, where J is the mechanical equivalent of heat,

$$\frac{C_p/C_v}{C_p/C_v - 1}\cdot\frac{JM\,(C_p - C_v)}{M}\cdot(T_0 - T) = gh$$

Or $$\frac{T_0 - T}{h} = \frac{g}{JC_p} = \frac{1}{10293} \qquad \dots (5)$$

Hence the temperature decreases proportionately with the height as we go upwards in the atmosphere.

The fall in temperature per km. is given by

$$T_0 - T = \frac{1 \times 1000 \times 100}{10293} = \frac{100000}{10293}$$
$$\approx 10°C$$

This is twice the actually observed value, *viz.* 5°C.

3. **Domestic and industrial applications.** (*a*) **Ventilation.** Convection plays an important part in the ventilation of rooms. A very simple method of ventilation is to establish convection currents between the outside air and the air in the room to be ventilated in such a way as to promote free circulation of the air without creating draughts. If there is a chimney above a fire in the room, hot air will continuously pass up the chimney and fresh cold air will pass into the room under the door or through the windows. Thus a fire in a room to which the outside air has access is a simple and effective means of ventilation. More complex and costlier methods of ventilation are electric fans and air-conditioning machines.

(*b*) **Domestic hot-water supply** also depends upon convection currents for its operation, as shown in Fig. 118. Water is heated in the boiler B, which is usually arranged at the back of the kitchen fire. The hot water proceeds along the upper exit pipe to the hot-water tank T kept in some cupboard. From T it goes up to the hot-water taps, P, P, P, in the various rooms, as indicated by the arrows. Cold, fresh and denser water from tank C enters the boiler B through T by the low entrance pipe, as indicated by the arrows. In this way, a continuous circulation of hot water in the rooms is kept up.

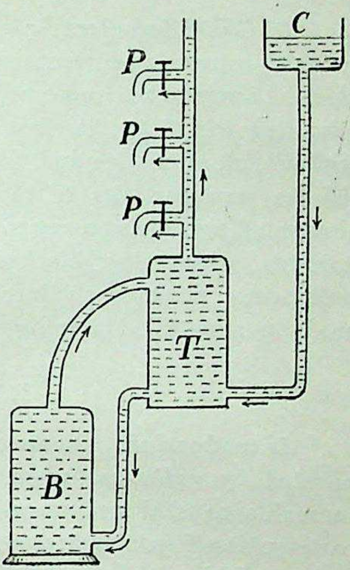


Fig. 118. Domestic hot-water supply.

(*c*) **Central heating.** Warming the rooms in winter is usually done by hot-water pipes which works on the same principle as the hot-water supply. The taps in the various rooms are replaced by "radiators", which are simply long pipes bent a number of times into *zig-zag* forms, through which the hot water of about 80°C flows from the *flow pipe* connected to the top of the boiler ; after feeding the radiators, the water returns by the *return pipe* to the boiler at its lowest point. The inlet of each radiator is connected to the flow pipe and the outlet to the return pipe. The cold water supply comes from the feed tank at the top of the building and enters the boiler at the lowest point. The feed tank is usually provided with a ball valve and an overflow outlet to maintain the level of water in it constant. Thus, the rooms of a house are heated by hot water raising and going through the radiator and cold water returning to the boiler to be heated in turn, *i.e.*, by establishing convection currents in water. Since the room is heated chiefly by convection of the air which takes place as the heated air rises continually from the hot radiator, "convectors" would be a more appropriate name for "radiators". It may be noted that steam or hot air is used instead of hot water in central heating of large buildings.

(*d*) **Radiators in automobile** work on the same principle of convection currents. The heated water from the cylinders of the engine flows up slanting pipes to the radiator, where it is cooled and passes down a lower pipe, entering the cylinder jacket again at the bottom.

(c) **Gas-filled electric lamps** contain a small quantity of argon in which convection currents are set up by the hot filament carrying the heat away to the upper part of the bulb. This results in a double advantage *viz.* (*i*) the filament can be heated to a higher temperature without risk of melting and thus brighter light can be obtained, and (*ii*) the tiny particles of the material of the filament which are thrown off are carried away to the top of the bulb by the convection currents, where they blacken the surface and eventually spoil the bulb ; since, however, the blackening is chiefly limited to the top of the bulb, a gas filled lamp has a longer life than the vacuum type.

RADIATION

Introduction. As already mentioned, heat is said to be propagated by *radiation*, when it is transmitted through vacuum or through a material medium without the medium playing an active part by itself getting heated. This statement needs further explanation. It does not mean that an intervening material medium will not be heated when thermal radiation falls on it or passes through it. As a matter of fact substances do absorb radiant heat to a greater or less degree when the latter falls on them or passes through them and thereby get heated to a more or less extent : *e.g.*, glass, wood, metal, etc. absorb radiant heat and become heated, while quartz, rock salt, fluorspar, etc. allow radiant heat to pass through without themselves being warmed to any great extent. This fact is used in the detection and measurement of the invisible thermal radiation, as we shall see below. Nor does it mean that no material medium is necessary for radiation, since the molecules of a material body, owing to their own heat vibrations act as the source of radiation, sending out waves that carry away energy.

The statement simply asserts that when heat is propagated by radiation, no material medium is necessary for the transmission and if a material medium intervenes, it is not necessary that it should first get itself heated as in the case of conduction and convection before it could assist at the propagation of thermal radiation. Further, since it can be shown that heat is a form of energy like light, the propagation of heat by radiation consists merely in a transference of energy that can take place even in empty space.

Concerning thermal radiation, the two important points that have been carefully investigated are :—

(*i*) *its intrinsic nature*, *i.e.*, its essential identity with light and other types of radiation,

(*ii*) *its dependence, as regards quantity and quality, on the nature and temperature of the radiating source.*

We shall therefore deal here only with these two main features of thermal radiation. For a detailed and quantitative study, we naturally require suitable radiating sources and efficient means of detecting and measuring the radiations emitted by the sources. Hence we shall first describe some of the important techniques devised for this purpose.

Sources of thermal radiation. Although any hot body maintained at a constant temperature can be used as a steady source of thermal radiation, two special devices known as the *Leslie cube* and the *black body* have been employed.

Leslie cube, devised by Leslie, is simply a hollow metal cube whose four vertical faces are coated with different substances, one lampblacked, the second painted white, the third polished and the fourth left untreated. The cube is so made that it can be rotated about a vertical axis. The cube when filled with hot water, becomes a source of radiant heat, with different radiating capacity or emissive power from the differently treated faces.

Black body. A perfectly black body is one which absorbs completely all the radiation which falls on it. As it neither reflects nor transmits any radiation it appears black, whatever be the colour of the incident radiation. The chief characteristic of such a body is that when heated to a suitable high temperature it emits *full* or *total* radiation. As it is a perfect absorber, it is also a perfect radiator, its emission being the greatest possible for every wavelength at any given temperature.

A lampblacked surface may be considered as perfectly black for all practical purposes. But other devices have been utilised to obtain a perfectly black body by different workers. Thus Lummer and Pringsheim used a carbon tube, 34 cm. long, 1·2 mm. thick and 1 cm. bore. The ends of the tube were covered by carbon-coated copper plates, which also served as leads for the heater coil wound round the tube. The tube was protected by layers of asbestos and fire-brick, but the slow oxidation of the tube by heat gradually rendered the tube less efficient.

Féry designed a perfectly black body, based on the principle that the radiation inside a uniformly heated enclosure is perfectly black, (first established by Kirchhoff, as we shall see below). Féry's black body, shown in Fig. 119, consists of a double walled hollow metallic sphere with a narrow opening O and lampblacked inside, nickel-polished outside. The interspace between the wall is evacuated to prevent loss of heat by conduction and convection. If radiations enter the sphere through the tiny hole O, they suffer multiple reflections on the inner wall and are completely absorbed. There is hardly any chance of the radiations getting out except by direct reflection from the surface opposite the hole. But even such an occurrence is almost entirely prevented by the conical projection P on the back wall opposite to the opening O. When used as a source of radiation, the spherical enclosure is heated in baths of fused salts. It is to be noted that the hole itself, not the walls of the enclosure, constitutes the perfectly black body. Hence, in using the arrangement care must be taken that only radiation issuing from the hole is allowed to reach the measuring instrument, which must be screened from radiation emitted from the walls of the enclosure.

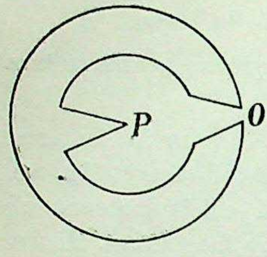


Fig. 119. Féry's black body.

Wien constructed a more convenient cylindrical type of black body, shown in Fig. 120, based on the same principle as Féry's. It consists of a cylindrical hollow metallic chamber C, electrically heated by a coil of thin platinum foil wound over it. The chamber is made of brass or platinum, depending upon the temperature to which it is raised. The inner surface of the chamber is blackened in order that the chamber may reach the equilibrium state quickly. The radiation from the chamber is limited by a number of blackened concave diaphragms D and emerges out of the hole H. The temperature of the chamber is measured by a thermocouple T. The cylinder

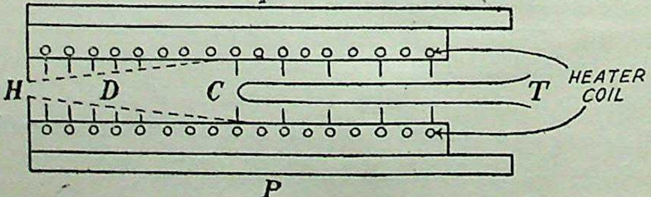


Fig. 120. Wien's blcak body.

is protected by concentric porcelain tubes PP with air space. This type of black body is now commonly used.

Instruments for detecting and measuring thermal radiation. The *basic principle* involved in the construction of instruments for detecting and measuring radiation may be stated as follows : Since radiation is merely a form of energy which can easily be converted into heat by making it fall on any body which can absorb it, the device must be capable of detecting and measuring a small quantity of heat. The *blackened bulb of an ordinary liquid thermometer*, which was used in the initial stages, was soon replaced by *Leslie's differential air thermometer* depending on the expansion of air when heated. *Crookes* devised a *radiometer* which functions on the mechanical force produced by the radiation on suitably mounted or suspended thin vanes. These were superseded by the *thermopile*, which works on the e.m.f. developed in a thermocouple when the junctions are at different temperatures. This instrument was brought to the highest degree of sensitiveness by *Boys* in his *radiomicrometer*, which is a combination of a thermocouple and a sensitive galvanometer. Another very sensitive instrument devised for measuring radiation is the *bolometer* which depends for its action on the change of resistance of platinum strips when heated by the incident radiation. We shall briefly describe these different instruments indicating their relative merits.

(*i*) **Leslie's differential air thermometer,** shown in Fig. 121, consists of two equal bulbs A and B containing air, connected by a U-tube which serves as a manometer with some non-volatile liquid like sulphuric acid in it. When one of the bulbs, say B, is exposed to the radiation, while the other, A, is shielded from the radiation, the air in B is heated and expands pushing the liquid in the manometer down. The difference in levels of the manometer thus created is a measure of the intensity of the incident radiation. This instrument is now only of historical interest and may be used for demonstration purposes.

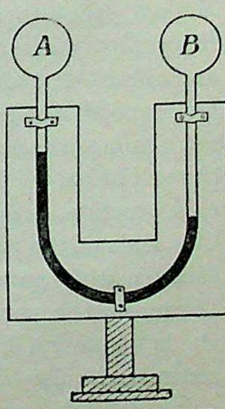


Fig. 121. Leslie's differential air-thermometer.

(*ii*) **Crookes' radiometer** is shown in Fig. 122. Two light aluminium rods RR, fixed at right angles in the form of a cross, carry at the free ends thin vertical vanes of mica or tin foil VV. The arrangement is suspended inside an evacuated glass vessel in such a way that it can rotate about a vertical axis. Similar faces of the vanes are coated with lamp black. When the radiation falls on these blackened faces, the vanes begin to rotate in such a direction that the blackened face continually recedes away from the source of radiation The cause of this rotation is readily understood. The blackened face absorbs the incident radiation and thereby gets heated, while the corresponding clear face remains at a lower temperature. The molecules bombarding the blackened face becomes more heated than the molecules bombarding the other face and in consequence they exert a greater pressure on the vane. This results in a net effective force repelling the vanes from the incident radiation. This is known as the *radiometer effect*. The velocity of rotation will be evidently a measure of the intensity of the incident radiation. Hence, suspending the vanes by means of a quartz fibre and observing the steady deflection produced under the influence of the radiation, the intensity of the radiation can be measured. Some workers have employed the radiometer for such measurements, but the instrument can at best be only a very sensitive detector, without any claim for accurate results in quantitative work.

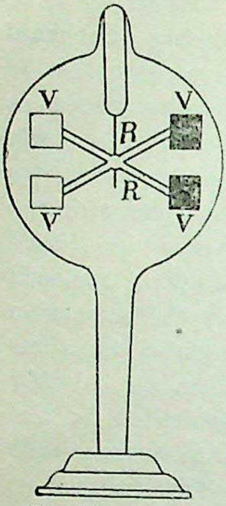


Fig. 122. Crookes' radiometer.

(*iii*) **Thermopile.** In the *original form*, as designed by Melloni, the thermopile consisted of a number of thermocouples made out of antimony and bismuth rods connected in series as shown in Fig. 123. One set, the hot junction, is exposed to the radiation, while the other, the cold junction, is suitably shielded. The ends of the pile are connected to a sensitive galvanometer. The thermoelectric current flows across the hot junction from bismuth to antimony. The deflection in the galvanometer caused by this current is a measure of the intensity of the incident radiation.

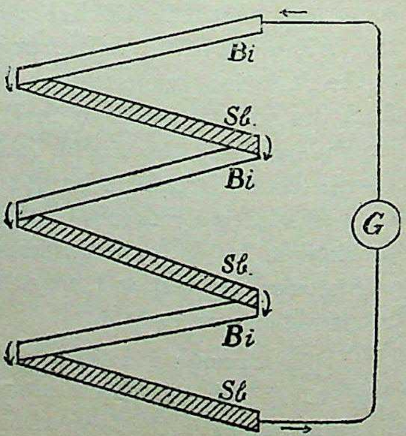


Fig. 123. Melloni's thermopile.

In the improved form in actual use, shown in Fig. 124, a large number of couples is used. The bars of antimony and bismuth are arranged to form a cube [Fig. 124 (*a*)], with all the hot junctions at one face and the cold junctions at the opposite face. The junctions are soldered, and the different layers are insulated with paraffined paper or mica. The face of hot junctions is coated with lamp-black and is also provided with a conical protector to prevent stray radiations from falling on it, while the cold face is covered with a metallic cap. [Fig. 124 (*b*)]. A rocksalt window is arranged in front of the hot face to let in the incident radiation. When not in use, the hot face is covered with a metallic cap.

When the hot face is exposed to radiation, the current enters at A in the bismuth bar and flows across the hot junction into the antimony bar and so on. Finally the current leaves the thermopile at B. Leads from A and B are connected to a sensitive galvanometer of low resistance with high voltage sensitivity. The instrument can be made direct reading by suitably calibrating the galvanometer. In the modern types of thermopile, the sesitiveness is very much increased by the following devices : (1) The sensitiveness evidently depends upon the number of thermocouples, but this cannot be increased indefinitely as the external resistance will increase. A compromise is therefore made by choosing the number of couples in such a way that the resistance of the thermopile is equal to that of the galvanometer. (2) Junctions and connecting wires are as thin as possible to minimise the loss of heat by conduction. (3) The pile is mounted in vacuum to avoid loss of heat by convection. (4) Suspended magnet (astatic) type of galvanometer is used.

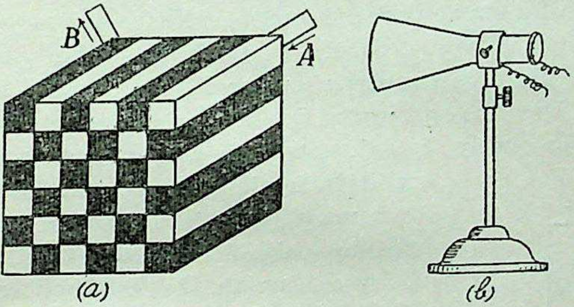


Fig. 124. Thermopile.

The *linear thermopile* which is employed in researches in the infra-red spectrum, consists of only a few pairs of thermocouples connected to a very sensitive galvanometer. The hot junctions are arranged to be along a vertical line. The elements of the couple are very fine wires wound on a small frame.

The chief drawback of the thermopile consists in the comparative slowness of its indication and the length of time required for it to return to zero.

(*iv*) **Boys' radiomicrometer,** shown in Fig. 125, consists of a single loop of fine copper or silver wire C to the lower ends of which two strips, one of antimony (Sb) and the other of bismuth (Bi), are attached. The lower ends of these strips are fixed to a thin copper disc D whose surface is blackened. The whole arrangement forms a thermoelectric circuit. When radiations fall on D, the lower junction of the Sb-Bi couple is heated and a current traverses the circuit. In order to detect this very small current the loop C is suspended between the poles of a strong permanent magnet NS, as in a suspended coil galvanometer. The top end of C is attached to a thin glass rod G carrying a light galvanometer mirror M, the glass rod itself being suspended by a fine quartz wire Q. The whole suspended system, which is extremely light, is enclosed in a thick brass case B to protect it from air currents. The Sb-Bi strips are arranged to be in a cavity of soft iron I in order to avoid disturbance due to the diamagnetism of bismuth. As the loop C, carrying the small current through the thermocouple induced by the radiation, is deflected in the magnetic field, the quartz fibre will be twisted, which is measured with the help of the mirror and a lamp and scale arrangement, so that the deflection of the spot of light on the scale is a measure of the intensity of the radiation incident on the disc D. The instrument can be made direct reading by suitable calibration. Thus it possesses all the advantages of an ideal thermopile of exceedingly small mass while the intensity of radiation is measured without the aid of a separate galvanometer.

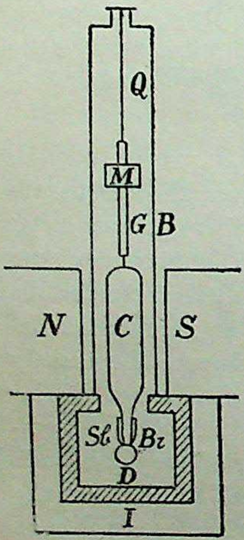


Fig. 125. Boys' radiomicrometer.

The merits of the radiomicrometer are: (*a*) extreme quickness of action, (*b*) freedom from extraneous thermal and magnetic disturbances, (*c*) constant and definite zero, given by the control of the quartz fibre suspension, (*d*) radiation may be limited by a narrow slit without seriously reducing the sensibility of the instrument, and (*e*) a quantity of heat as small as $1/150,000^{th}$ of that received from the full moon can be detected with certainty. The chief drawback is that it must, like a suspended coil galvanometer, be kept in a fixed position and cannot be used in other than the horizontal direction so that in this respect it is less convenient than the thermopile and the bolometer.

(*v*) **Bolometer.** Langley was the first to utilise the uniform change of resistance of a platinum strip with temperature to construct a very sensitive instrument for measuring thermal radiation and he called it the bolometer. It consists essentially of very thin platinum strips, of 1 to 2×10^{-3} mm. thickness, joined together in series, resembling a grating or a grid of parallel elements, as shown in Fig. 126, and suitably mounted in a frame of slate. The strips are coated with platinum black, in order that they may absorb as much as possible of the radiation falling on them. A grid so constructed has an appreciable amount of resistance (about 50 ohms) but a low thermal capacity for the given surface area, which makes the bolometer to reach its equilibrium position in the shortest possible time when exposed to radiation. The grid is enclosed in a long tube to protect it from air currents and the radiation is allowed to fall on it only after passing through a number of apertures.

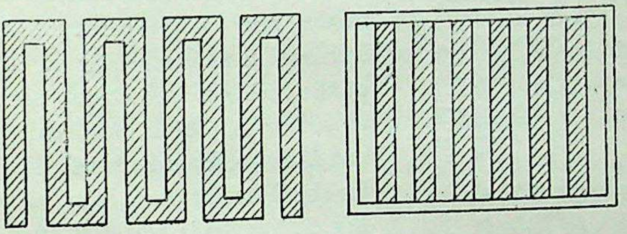


Fig. 126. Bolometer.

Two such grids, identical, are used, one exposed to the radiation and other well screened from all radiation. The two grids are arranged to form the two ratio arms of a Wheatstone bridge. Before exposure to the radiation, the two other arms of the bridge are adjusted for balance, so that there is no deflection in the galvanometer. If the radiation is now allowed to fall on the grid meant for that purpose, the resistance of the grid increases instantaneously, the balance is upset and the galvanometer records a deflection. A change of temperature of 0·0001°C produces a measurable deflection. Measuring the increase in resistance, it is possible to calculate the intensity of the incident radiation. Langley used his bolometer to measure the intensity of the radiation reaching us from the moon.

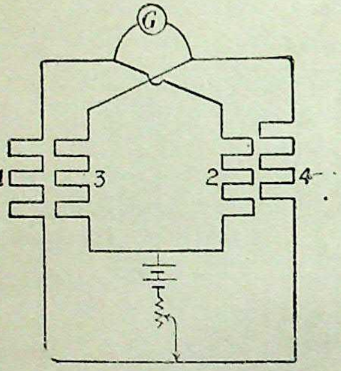


Fig. 127. Lummer-Kurlbaum bolometer arrangement.

Lummer and Kurlbaum improved the bolometer of Langley into an extremely sensitive and delicate instrument by the following devices : (*i*) Since the sensitiveness depends on the thinness of the platinum strips, (the thinner the strips, the larger is the rise in temperature and the increase in resistance for given amount of the incident radiation) strips only 0·0005 mm. thick, are used. (*ii*) Instead of two, four identical grids are used for the Wheatstone bridge, as shown in Fig. 127. Grids 1 and 3, put in the opposite arms of the bridge, are so arranged one behind the other that the strips of 3 cover up the gaps in 1 and thus receive the radiation passing between the strips in 1. By this device, twice as much radiation falls on the bolometer as with a single grid, so that the effect is doubled. The other two grids shielded from radiation are arranged in the remaining two arms 2 and 4 of the bridge. The bridge is first balanced with all the four grids shielded from the radiation. The grids 1 and 3 are then exposed to the radiation, when the balance is upset and the galvanometer shows a deflection corresponding to a change of resistance equal to twice that would have been obtained in Langley's technique. (*iii*) The sensitiveness of the instrument is further increased by using a very sensitive galvanometer.

A linear *type of bolometer* with a single narrow strip has also been successfully employed in the study of the distribution of heat in the solar spectrum.

Due to the extreme thinness of the strips the bolometer reacts much more promptly to radiation than the thermopile. It has also the advantage over the radiomicrometer in that it can be readily shifted from place to place. However, it is now rather rarely used since the modern types of thermopile are often preferred.

Nature of thermal radiation—its essential identity with light. Since light and heat from the sun reach us at the same time and during a total solar eclipse heat is cut off simultaneously with light, it has been recognised quite early that light and thermal radiation are similar, both obeying the same general laws. With the introduction of suitable sources of thermal radiation, and instruments for detecting and measuring such radiation, experiments were conducted to verify the above general opinion and see how far the similarity between radiant heat and light could be justified, which led to a final and complete admission of their essentially identical nature. We shall now briefly describe some of the important properties of thermal radiation established by such investigations :—

(*i*) **Thermal radiation travels through empty space with the velocity of light.** This follows readily from the observations that the sun's heat and light reach us at the same time and are cut off together during a solar eclipse. That thermal radiation can travel through vacuum is made evident also by the fact that we are able to receive heat from a highly evacuated electric lamp. Even when a very small current passes through the filament which is not sufficient for the filament to glow, the thermal radiation can be detected with a sensitive thermopile.

(*ii*) **Thermal radiation, like light, travels in straight lines,** since, for instance, the heat coming from a flame can be cut off by interposing a screen just enough to cut off the light. On replacing the flame by a hot non-luminous source, no heating effect can be detected by a thermopile.

(*iii*) **Thermal radiation obeys the law of inverse squares, like light.** This can be experimentally established by the simple arrangement shown in Fig. 128. C is a Leslie cube containing hot water. The thermopile T is presented to the lamp-blacked face of C at various distances. If the thermopile is moved from a position T to another T′ which is, say, double the distance of T from the face of the cube, the deflection of the galvanometer connected to the thermopile is unchanged, consistent with the inverse square law. For, the area of the surface of C from which radiation reaches the thermopile at T′ is increased four times, and as the amount of radiation reaching the thermopile remains the same, the intensity of radiation must have been reduced to one-fourth of that in the first position T. This means that the intensity of radiation varies inversely as the square of the distance. For the same reason, the deflection of the galvanometer is found independent of the distance of the thermopile from the cube over a moderate range, *i.e.*, till the face is big enough to contain the circle projected on it from the thermopile.

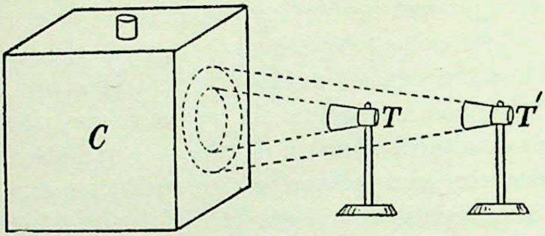


Fig. 128. The inverse square law.

(*iv*) **Thermal radiation is reflected according to the same laws as light.** To show that the angle of incidence is equal to that of reflection for thermal radiation, the arrangement shown in Fig. 129 may be used. M is the plane mirror of a speculum metal. Two tubes are arranged in front of M, so that their axes are inclined to M. A source of thermal radiation, F, say a white-hot platinum foil, is placed in front of one of the tubes and a thermopile T in front of the other. A screen S cuts off all direct radiation from F to T. It is found that the galvanometer connected to the thermopile shows a large deflection only when the mirror is so turned that the angle of incidence is equal to the angle of reflection.

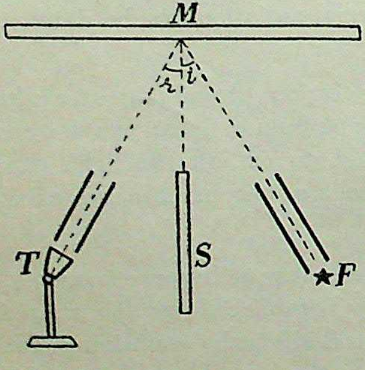


Fig. 129. Laws of reflection for thermal radiation.

The laws of reflection can be further verified by arranging two parabolic mirrors at some distance apart on a common axis and placing a hot platinum foil at the focal point of one of them. When a thermopile is placed at the focus of the other, a large deflection is produced in the galvanometer attached to the thermopile, while the deflection decreases as the thermopile is moved out of the focus. This shows that thermal radiation obeys all the laws of geometrical optics.

(*v*) **Thermal radiation is refracted like light.** This is made evident by the following simple experiment, first carried out by Herschel. A spectrum of sunlight is produced by means of a prism and thrown on a screen. A thermometer with its bulb coated with lamp-black is moved across the spectrum. When it is near the violet end of the spectrum, very little effect is noticed, but as the red end is approached, it begins to record a rise in temperature, and this effect continues even beyond the red end where no visible radiations are falling on it. It is then receiving invisible thermal radiations only and is said to be in the infra-red region of the spectrum. Thus Herschel discovered the infra-red part of the solar spectrum and showed that it was continuous with the visible spectrum. Thermal radiation therefore can be not only deviated but also split up into a spectrum, like light.

(*vi*) **Thermal radiation exhibits the phenomena of interference and diffraction.** Diffraction can be readily observed with the help of a concave grating or using a transmission grating made up of a number of equidistant parallel wires. This brings out the wave nature of thermal radiation as in the case of light.

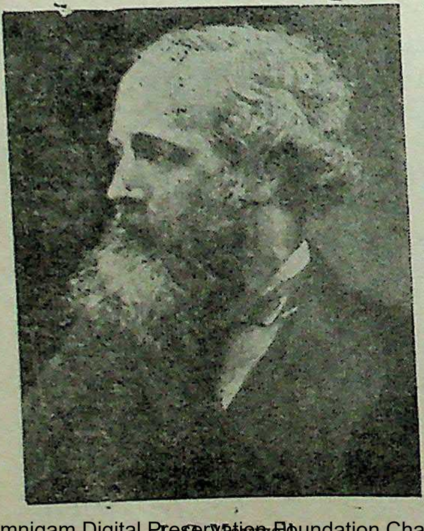
(*vii*) **Thermal radiation can also be polarised like light.** For instance, if light from an incandescent lamp is made to traverse two similar plates of tourmaline, the image is found to vanish on rotating one of the plates. Now replacing the lamp by a Leslie cube, a thermopile placed in the position occupied by the image records no deflection ; but if one of the plates is rotated a deflection is observed. This shows that the radiation waves, like light waves, are *transverse* in nature.

All these observations lead to the conclusion that thermal radiation is identical with light, both being essentially of the same nature and propagated as radiant energy in the form of transverse waves with the same velocity through space. They can be differentiated only by the difference in their frequency and wavelength, visible light having frequencies in the range between 8×10^{14} and 4×10^{14}, while thermal radiation is limited to the range 4×10^{14} to 3×10^{11}, occupying the infra-red region of the spectrum. The infra-red rays are not visible to the eye, but their presence is readily detected by their heating effect. They are generally considered as radiant heat rays, but this does not mean that the rays in the visible region do not radiate heat. They all do, but the infra-red rays have greater heating capacity, while the visible rays have greater luminosity.

More recent work has resulted in the discovery of other forms of radiation such as the Hertzian waves of still longer wavelengths than the infra-red, the ultra-violet, X-rays, γ-rays and cosmic rays beyond the visible violet region in the decreasing order of wavelengths. It has also been shown that all these different types of radiation have essentially the same nature as thermal radiation and visible light. Hence the general name "*radiation* or *radiant energy*" is now used to designate all of them.

At one time it was thought that some medium must be postulated in which the waves, that constitute the radiant energy, are propagated. It was called *ether* and was supposed to fill all space and penetrate all matter. But it was soon realisedt hat such a medium had to possess contradictory properties, if it were to account adequately for the very high velocity of radiant energy (3×10^{10} cms./sec.) on the one hand and the transverse wave motion involved in the production of radiant energy on the other.

Maxwell in his famous **electromagnetic wave theory of light** was able to overcome the difficulty to a great extent by showing that radiation results not from the mechanical vibrations of the particles of ether, but from the vibrations of the inseparably connected electric and magnetic fields of a "displacement current" in the medium. He was also able to achieve a marvellous synthesis of all the different types of radiations on the basis that all of them are electromagnetic waves arising from the periodic motion of electric charges, contained by the molecules and atoms of the source of radiation. The radiations cover a very wide range of frequencies in wavelengths (depending upon the



J. C. Maxwell

quickness of alternation of the displacement currents) which form a long gamut, known as the *electromagnetic spectrum*, indicated below :—

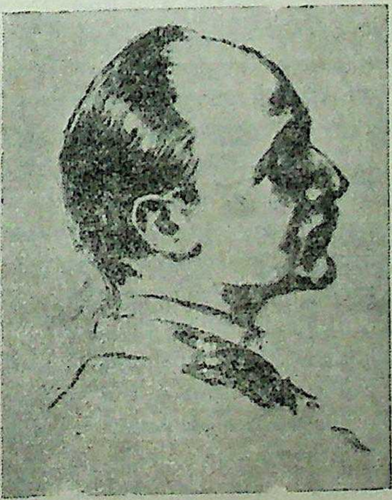
Rays	*Frequency*	*Wavelength*
Cosmic rays	$\sim 10^{23}$	$\sim 10^{-11}$ cm.
γ-rays	6×10^{20} to 10^{18}	10^{-10} to 10^{-8} cm.
X-rays	6×10^{19} to 6×10^{15}	10^{-9} to 10^{-6} cm.
Ultra-violet	2×10^{16} to 8×10^{14}	$1{\cdot}4\times10^{-6}$ to 4×10^{-5} cm.
Visible	8×10^{14} to 4×10^{14}	4×10^{-5} to 8×10^{-5} cm.
Infra-red	4×10^{14} to 3×10^{11}	8×10^{-5} to 0·04 cm.
Hertzian waves	10^{13} to 10^{3}	0·01 cm. to 100 km.

From this chart it is seen that the essentially same electromagnetic radiation is called by different names according to the different ranges of frequency and the corresponding wavelengths involved. It is to be noted that there is an overlapping of limits as regards the frequencies or wavelengths of the different types of radiation. Further, all of them are propagated with the same velocity through space and all consist of alternating electric and magnetic fields. This wonderful unification of all types of radiation—visible and invisible, weak and strong, thermal, optic, electric and magnetic—is one of the great achievements of Maxwell's electromagnetic theory, which is bound to last.

Max Planck discovered a novel aspect of these radiations which is known as the **quantum theory of radiations.** According to it, the radiant energy of a system or the exchange of radiant energy between different systems occurs not in a continuous fashion , as demanded by Maxwell's electromagnetic wave theory, but *in a discrete quantified form, as integral multiples of an elementary quantum of energy* ε, represented by the relation

$$\varepsilon = h\nu$$

when ν is the frequency of the radiation and h the Planck's constant. This means that *radiant energy should be considered atomic in structure, like matter.*



Max Planck

Einstein was obliged to admit

such a conception in the case of light in connection with his *theory of relativity,* where the hypothetical medium, ether, the essential support of light waves, had to be set aside as futile in the interpretation of physical phenomena. As a matter of fact, all experiments designed to detect the ether directly have so far failed. Hence, many scientists at the present day have given up the idea of postulating ether even as a mere carrier of electromagnetic waves and have preferred to interpret electromagnetic phenomena in terms of what is known as "waves of probability", deduced from another recent novel theory known as "*matter waves*", into the details of which we cannot enter here.

Having thus analysed the intrinsic complex nature of radiations in general and of thermal radiation in particular, with which we are directly concerned here, we shall now turn our attention to the second main feature of thermal radiation, *viz.*, how its quantity and quality depend upon the nature and temperature of the source itself.

Dependence of the quantity and quality of thermal radiation on the nature and temperature of the source. The study of this problem is based on certain essential characteristics of the process of radiation, such as *emission and absorption, Prevost's theory of exchange* and *radiation in a uniform temperature enclosure,* which therefore have to be considered first.

Emission and absorption of radiation. Every hot body emits thermal radiation from its surface, which depends upon the nature of the surface, its size and the nature of the surroundings. This is known as *emission* and is estimated by a quantity known as the *emissive power*, which may be defined for the present purpose as the amount of radiation emitted per sq. cm. per sec. at a given temperature. So defined, the emissive power depends only on the nature of the surface. The emissive power of different surfaces was investigated by Leslie employing a Leslie cube as the source and a thermopile to measure the radiation. With the lamp-blacked surface of the cube facing the thermopile, the deflection of the galvanometer connected to the thermopile, which is a measure of the amount of radiation falling on the thermopile per second, is noted. Similarly the other surfaces, untreated, painted white and polished are made to face the thermopile and the deflection in each case is observed. It is found that the lamp-blacked, untreated, painted white and polished surfaces have emissive powers in the descending order, the first having the highest, while the last the least. The emissive powers of some surfaces are given here for comparison :—

Lampblack ...	98%
Indian ink ...	88%
Platinum ...	11%
Copper ...	5%
Silver ...	2 to 3%

When the emitted radiation falls on matter, a part of it is *reflected*, another part *absorbed*, while the remainder is *transmitted*. The coefficients of reflection, absorption and transmission are connected by the relation

$$r + a + t = 1$$

where r is the fraction of the incident total radiation which is reflected, a the fraction which is absorbed and t the fraction transmitted.

If we put $r = 0$, $t = 0$ in the above relation, we get $a = 1$ and this defines a *perfectly black body* which neither reflects nor transmits, but absorbs all the radiation that falls on it, so that it appears black. Lamp-black is the nearest approach to the ideal black body, as it absorbs about 98% of the incident radiation.

The *absorptive power* of different surfaces may be compared by the following method. The bulb of a thermometer is coated with one of the substances to be tested, say lamp-black, heated to the highest temperature at which it is to be used and then placed in open air to cool. Its temperature is noted at regular intervals of time and the cooling curve is drawn. The thermometer is now mounted at the suitable distance from a given source of radiation, which is focused on the bulb by a lens. The blackened bulb will absorb a certain fraction of the radiation which falls on it and this will raise its temperature until it is so hot that it loses as much heat by cooling as it is absorbing from the incident radiation. The steady temperature so attained is noted, and from the cooling curve, the rate of fall of temperature θ_1 at this temperature is found. The experiment is repeated in a similar manner with the bulb coated with the other substances to be tested and the rates of fall of temperature at the respective steady temperatures can be found from the corresponding cooling curves. For instance, with the bulb silvered, let θ_2 be the rate of fall of temperature.

If w is the water equivalent of the bulb, the amount of radiation absorbed by the bulb lamp-blacked $= w\theta_1$ and the corresponding amount for the bulb silvered $= w\theta_2$.

Since the amount of radiation falling on the bulb in all the cases is the same, the ratio of the absorptive powers of lamp-black and silver surface $= \dfrac{w\theta_1}{w\theta_2} = \dfrac{\theta_1}{\theta_2}$.

The absorptive powers of a few substances are given here :—

Lamp-black	...	98%
Indian ink	...	85%
Shellac	...	72%
Dull copper	...	13%

The results obtained indicate a very interesting point, *viz.*, if the surfaces are arranged in the order of decreasing emissive power, say as lamp-black, untreated, painted white and polished, that is also the order for the absorptive power, lamp-black having the maximum absorptive power, while the polished surface the minimum absorptive power. This means, in other words, that *substances which are good emitters are also good absorbers, while bad emitters are bad absorbers.* At first sight, this might appear contradictory. But it is not so, since we are dealing here not with the net gain or loss of heat observed, but with the total absorption, quite apart from what the substance may be emitting at the same time, and with the total emission, quite apart from what the substance may be absorbing at the same time. One consequence of this state of affairs is that all bodies ultimately reach the same temperature when exposed to the same radiation, provided they can gain or lose heat by radiation. This condition, however, is not ordinarily realised in practice, since bodies do not find themselves in a vacuum and hence most of the loss of heat is due to conduction and convection in the surrounding air.

The *reflecting power* of different substances can be easily found by allowing the radiation from a Leslie cube to fall on the surface of the substance under test and receiving the reflected radiation in a thermopile. Next the thermopile is placed in the position occupied by the reflecting surface. The ratio of the deflections in the two cases gives the reflecting power.

The *transmitting power* of substances as regards thermal radiation is called by a special name, *diathermancy*, which is analogous to transparency in the case of light. Substances which allow thermal radiation to pass through them are called *diathermanous*, while those which do not *athermanous*. Early experiments performed by Melloni and Tyndall to study this property used the following simple technique : Direct radiation from a Leslie cube is allowed to fall on a thermopile and the deflection is noted ; the substance under test is interposed between the radiation and the thermopile and the deflection again noted. The ratio of the two deflections gives the diathermancy or transmission coefficient of the substance. Solids, liquids and gases can be studied in this manner. The best diathermanous solids are rock salt, sylvine, quartz and certain other crystals. Pure air is highly diathermanous, but water vapour and carbon dioxide are athermanous.

Note : The emissive and absorptive powers of surfaces are often estimated by comparing their emissivity and absorption with those of a perfectly black body.

The *emissivity* of a given surface is defined as the quantity of heat radiated per second by one square centimetre of its surface when its temperature is 1°C above the surroundings. If E and E′ be the emissivities of a surface with and without lamp-black respectively, under identical conditions of temperature, the *emissive power* of the surface is given by

$$e = \frac{E'}{E}$$

It is here assumed that the surface when lamp-blacked becomes perfectly black. It is evident that the emissive power of a perfectly black surface is unity.

The *absorptive power* of a surface can be obtained in a similar manner by comparing its absorption with that of a perfectly black surface under the same conditions. Since, however, a perfectly black surface absorbs all the thermal radiation falling on it the absorptive power of any surface is given by the ratio of the amount of heat absorbed by it in a given time to the total amount of heat incident normally on it in the same time. If Q calories fall on the surface and Q′ calories out of it are absorbed, the absorptive power of the surface is given by

$$a = \frac{Q'}{Q}$$

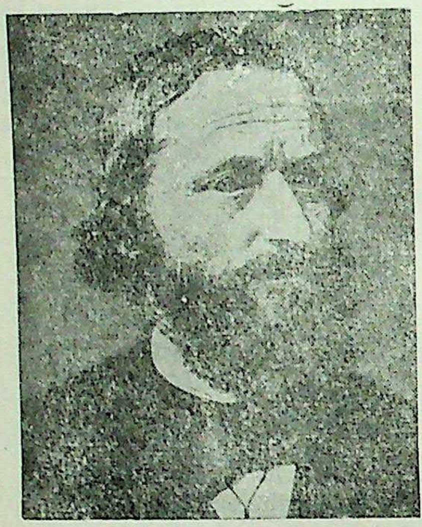
Prevost's theory of exchange. Since fire produces sensation of warmth, while a block of ice that of cold, the idea that hot bodies emit hot radiations and cold bodies emit cold radiations was prevalent for some time, until, in 1792, Prevost pointed out that such a conception was incorrect and proved that thermal radiation was essentially an exchange process. His line of argument was as follows. A body, when placed even in a vacuum, cools down to the temperature of the surroundings, after which its temperature remains constant. What causes the hot body to start radiating when it is placed in the enclosure ? How can the surroundings have any influence on it when they are separated from it by a finite amount of empty space ? Why does the body stop radiating when it reaches the temperature of the surrounding ? If one were to admit that radiation can take place only between two bodies at different temperatures, then one is obliged to admit that the temperature of the surroundings has to influence the hot body in spite of the empty space which means 'action at a distance' that is repugnant to scientific thought. Hence it is to be presumed that *all bodies at all temperatures above the absolute zero are continually radiating, the amount increasing with temperature, unaffected by the presence of surrounding bodies. The rise or fall of temperature which is observed in a body is due to its exchange of radiant energy with the surrounding bodies. This is known as Prevost's theory of exchange.*

A hot body, according to this conception, radiaties more heat to surroundings than it absorbs from that received by it from the surroundings. As a result, it loses heat and cools down. This continues until it reaches the same temperature as its surroundings when it radiates as much as it absorbs. This thermal equilibrium is *dynamic not static.* Likewise, the warmth felt before a fire is due to the fact that our body is receiving more heat energy from the fire than it is losing by its own radiation. The sensation of cold produced by a block of ice is similarly due to the fact that our body being at a higher temperature loses more energy by radiation than it receives from the ice which is at a much lower temperature. A body will cease to emit radiation only when it is at the absolute zero. The soundness of this theory is evident not only because it adequately explains observed facts, but also because it is based on the legitimate assumption that bodies whose molecules are in motion must continually radiate and molecular motion ceases only at the absolute zero.

Radiation in a uniform temperature enclosure. When different substances of different colours are heated together in a red-hot crucible, maintained at a uniform temperature, they all lose their individual colours and appear red, and hence are indistinguishable. When they are quickly removed from the crucible and examined in a dark room, they exhibit their proper colours but when in the crucible only one colour, caused by the temperature of red heat. From this one may conclude that all bodies radiate in the same way within an enclosure at a uniform temperature. A body within such an enclosure emits radiations precisely similar to those which it receives and will not be changed in character by altering the material of the walls of the enclosure or by the pressure of other bodies. Hence *the radiation within a uniform temperature enclosure depends only on the temperature and is entirely independent of the nature of the walls or of the presence of any body in the enclosure.* A rigorous proof of this conclusion can be obtained on the principles of thermodynamics, as will be indicated in a later chapter. What has been shown above for radiation as a whole holds good also for radiation per unit volume which is called the *energy density* and for each of the infinitesimal bands of wavelength into which the radiation can be divided. Hence *the energy density associated with each wavelength in a uniform temperature enclosure depends only on its temperature.*

We have seen above that although all bodies lose their characteristic radiating peculiarities while they are in the red-hot crucible, they resume those peculiarities when taken out and examined in the dark. A perfectly black body, however, will exhibit the same brightness within the crucible and outside in the dark. Because, being opaque and non-reflective, all the radiation it gives out in the enclosure is proper to itself ; it therefore retains them even when outside the crucible. Further, since a perfectly black body is one which absorbs all the radiations that fall on it, of whatever wavelength they may be, the radiations emitted by it will possess a character independent of the property of any particular substance, solely dependent on the temperature to which it is raised ; in other words, the interchange of energy between the perfectly black body and the surrounding space in which it is situated will lead to the establishment and maintenance of a state of equilibrium completely defined by the temperature. Hence *the radiations of a perfectly black body will be identical in every respect with those within a uniform temperature enclosure, so that the latter are often called black body radiation.* Moreover, since a black body has the maximum absorbing power for every wavelength, its emission also is the greatest possible for every wavelength at any given temperature. So the radiation it emits and that inside a uniform temperature enclosure are also known as *full or total radiation.*

Kirchhoff was the first, in 1858, to establish this essential identity of the radiation of a black body with that of a uniform temperature enclosure. Later, in 1895, Féry, Wien and Lummer utilised this fact to construct black bodies for experimental purposes, as we have already seen.



Kirchhoff

Having thus considered the basic features of thermal radiation, let us now take up the problem of the dependence of thermal radiation on the nature and temperature of the source. Different workers tackled it in the following different ways : Kirchhoff, in 1859, established a relation between the emissive and absorptive powers of a substance at any given temperature which is known as *Kirchhoff's law*. In 1884, Stefan and Boltzmann were able to arive at another important conclusion about the dependence of the total radiation from a black body on temperature, generally known as the *Stefan-Boltzmann law*. A special interest was attached to the spectral distribution of energy in the radiation emitted by a black body : *How is the energy distributed among the various wavelengths in the black body spectrum and at what wavelength is most of the energy emitted ?* Investigations on this point led progressively to different results, such as *Wien's law* (1893), *Rayleigh-Jeans law* (1900) and *Planck's law* (1901). While the fist two of these laws fitted in with experimental data only partially, the last one met with complete success, and developed, contrary to the classical electromagnetic theory of radiation, into the modern quantum theory. We shall here briefly state how these various attempts were made, without entering into details which are beyond the scope of the book.

Kirchhoff's law. We have seen above that the nitial researches on the emission and absorption of thermal radiation showed that they vary in a similar manner, good emitters being also good absorbers and bad emitters bad absorbers. In 1859, Kirchhoff deduced from such observations an important law which may be stated as follows : *At any given temperature and for radiations of the same wave-length the ratio of the emissive power to the absorptive power is the same for all substances and is equal to the emissive power of a perfectly black body.*

Kirchhoff's own proof of the law is somewhat complicated. A much simpler proof can be had in the following manner, based on the fundamental characteristics of thermal radiation explained in the previous pages.

Let us consider a body placed inside a uniformly heated enclosure maintained at temperature T. The radiation within the enclosure will be independent of the nature of the walls of the enclosure and of the presence of the body.

Let dQ be the quantity of radiant energy, of wavelength lying between λ and $\lambda + d\lambda$, falling on the body per unit area of its surface per second. Let a_λ be the *absorptive power* of the body ; a_λ is the ratio of the radiant energy absorbed by the body to the total incident energy at the temperature T and for the wavelength λ. Then the amount of radiant energy absorbed by the body per unit area per second is $a_\lambda\, dQ$. The remainder $(1 - a_\lambda)\, dQ$ is reflected or transmitted.

If e_λ be the *emissive power* of the body, the amount of energy radiated per unit area per second under the same conditions of temperature and wavelength, is $e_\lambda\, d\lambda$. Hence the total energy given out by the body per unit area per second is $(1 - a_\lambda)\, dQ + e_\lambda\, d\lambda$.

Since the body is in temperature equilibrium with the enclosure, the radiant energy given out must be equal to that received.

$$\therefore \quad dQ = (1 - a_\lambda)\, dQ + e_\lambda\, d\lambda$$

$$\text{Or} \quad a_\lambda\, dQ = e_\lambda\, d\lambda \qquad \ldots (1)$$

For a perfectly black body, since $a_\lambda = 1$ and e_λ has a maximum value, which we may denote by E_λ,

$$dQ = E_\lambda\, d_\lambda \qquad \ldots (2)$$

Substituting this value of dQ in (1) we have

$$a_\lambda E_\lambda\, d\lambda = e_\lambda\, d\lambda$$

$$\text{Or} \quad \frac{e_\lambda}{a_\lambda} = E_\lambda \qquad \ldots (3)$$

This relation (3) shows that, at any given temperature T and for radiations of the same wavelength λ, the ratio of the emissive power to the absorptive power of a substance is constant and equal to the emissive power of a perfectly black body. This is Kirchhoff's law which is here proved for bodies inside a uniform temperature enclosure. Since, however, the emissive and absorptive powers depend only on the nature of the body and not on its surroundings, it follows that the law is general, holding good under all conditions for pure temperature radiation.

In the above relation, since E_λ is a constant, if e_λ is large a_λ also is large and *vice versa*. This shows *that good emitters are also good absorbers.*

Experimental verification of Kirchhoff's law. Ritchie, demonstrating with the following simple arrangement that good emitters are also good absorbers, was able to confirm experimentally Kirchhoff's law. Two equal cylindrical metal vessels A and B containing air are connected to a manometer M as shown in Fig. 130. Another long cylindrical metallic vessel C of the same cross-sectional area as A and B is arranged between A and B, mounted on a pillar in such a way that it can be rotated. The face of C on the side of A is coated with lamp-black, while the other face on the side of B is polished. The faces of A and B which are turned towards C are polished and lamp-blacked respectively. When the vessel C is filled with boiling water, it is found that the levels in the two limbs of the manometer are the same, indicating that A and B are at the same temperature. In other words, the amounts of energy received by them from C are equal, the polished face of A absorbing a fraction of the radiation emitted by the blackened face of C and the blackened face of B absorbing completely the fraction emitted by the polished face of C.

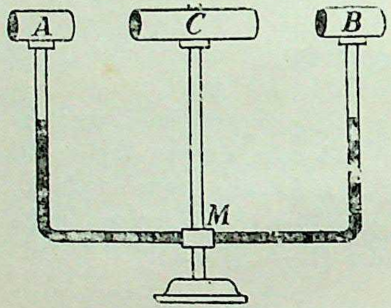


Fig. 130. Ritchie's apparatus.

If C is now rotated so that its blackened face is turned towards the blackened face of B and its polished face is opposite to the polished face of A, a difference in level is observed in the manometer, because now a good absorber is opposite to a good emitter and a bad absorber opposite to a bad emitter.

Considering the first case where the levels in the manometer are the same, let e_1 and e_2 be the energies emitted per second by the blackened and polished faces respectively. Similarly, let a_1 and a_2

be the fractions of the incident energy absorbed by the same faces respectively.

The energy emitted per second by the blackened face of C = e_1. If k is the fraction of the total energy emitted by C, falling on the face of A, the energy incident on the polished face of A per second $= ke_1$ and the energy absorbed by the polished face of A per second $= ke_1a_2$. Similarly the energy absorbed by the blackened face of B $= ke_2a_1$.

But $ke_1a_2 = ke_2a_1$, since the amount of energy absorbed by A and B are equal.

$$\therefore \qquad \frac{e_1}{a_1} = \frac{e_2}{a_2} = \text{constant.}$$

This shows that good emitters are good absorbers and thereby verifies Kirchhoff's law.

Illustrations of Kirchhoff's law. If a piece of china with some dark paintings on it is heated in a furnace to a high temperature (about 1000°C) and then taken out quickly and examined in a dark room, the dark paintings appear much brighter than the white portion, because the paintings being better absorbers, emit also much greater light. The silvered surface of a thermos flask does not absorb very much heat from outside and hence preserves ice from melting quickly ; it also does not radiate too much heat from inside and hence preserves hot liquids for a considerable time. There are many such cases illustrating Kirchhoff's law, but the one classical example regarding the explanation of the *Fraunhofer lines* in the solar spectrum given by Kirchhoff on the basis of his law deserves special mention.

Fraunhofer was the first, in 1801, to discover a large number of dark lines in the solar spectrum. Although he carfully measured their wavelengths, realising their importance, he was unable to explain how they originated. He also investigated the light from stars and found similar dark lines in their spectra.

Other workers, notably Fizeau, found that, if the solar spectrum was examined side by side with the spectrum from a sodium flame, the two yellow lines of the sodium spectrum occupied the same place as the Fraunhofer D-lines in the solar spectrum. A similar coincidence was also observed in the case of the hydrogen spectrum. Although these facts paved the way for a possible solution, the dark lines of Fraunhofer remained unexplained, until Kirchhoff completely solved the problem on the basis of his law as follows :—

Since sodium can emit the D-lines when it is excited, it can also absorb the same light when white light falls on it and produce the corresponding dark lines. As a matter of fact, when white light from an arc lamp is passed through relatively cool sodium vapour and analysed in a spectrometer, the spectrum is found to be crossed by two dark lines in precisely the same position as the yellow lines in the emission spectrum of sodium. This suggests a correct explanation of the Fraunhofer lines in the solar spectrum. The light from the central mass of the sun is such that it emits a continuous spectrum without dark lines. But this light has to pass though a cooler atmosphere containing a number of elements, such as H_2, N_2, O_2, Na, Cu, etc. in the gaseous form, which absorb effectively the lines that they themselves can emit and thus give rise to the Fraunhofer lines. The presence of dark lines in the spectra of stars is accounted for in a similar manner. It is by the analysis of such dark lines, one is able to tell of what elements the cool atmosphere surrounding the sun and stars are composed.

Kirchhoff's discovery is of much greater importance than the mere success in explaining the dark absorption lines in solar and stellar spectra would indicate. For it clearly shows that every type of atom, when properly excited, emits light of definite wavelength which is characteristic of the atom.

Stefan-Boltzmann law. Newton was the first to study in a systematic manner the relation between the heat radiated by a body in a given enclosure and its temperature. A large bulbed mercury thermometer was heated until the mercury thread reached a good height in the stem. The bulb was then enclosed in an evacuated flask, the walls of which were blackened inside and were maintained at a fixed temperature by means of a suitable bath. The rate of fall of temperature was observed and was taken to give the rate at which heat was radiated from the bulb. When a graph was plotted with the rate of fall of temperature $(-d\theta/dt)$ as ordinate and the excess of temperature $(\theta - \theta_0)$, where θ is the temperature of the hot bulb and θ_0 the temperature of the enclosure, as abscissa, a straight line was obtained. Hence $(-d\theta/dt) = k\ (\theta - \theta_0)$ ...(1) which is *Newton's law of cooling*.

As already noted, this law holds good for small differences of temperature. Further, when it is used in practice, for instance, for radiation correction in calorimetric measurements, convection effects predominate, to avoid which precisely the bulb is placed in an evacuated enclosure in the experiment described above. Even with this precaution taken to study the radiation effect alone, considerable deviations from the law occur when the temperature difference exceeds 40°C.

Dulong and Petit, with the aim of obtaining a more general law that will hold for any difference of temperature, however great, conducted an elaborate series of experiments on the rate of cooling of a hot body. They found that their results could be expressed by a relation of the form

$$V = k\,\{ f(\theta) - f(\theta_0) \} \qquad \ldots (2)$$

where V is the rate of loss of temperature of the hot body when it is at a temperature θ°C in an enclosure maintained at θ_0°C.

They further found that $f(\theta)$ must be an exponential function for satisfactorily fitting their results and hence gave the final formula as

$$V = k\,(a^{\theta} - a^{\theta_0}) \qquad \ldots (3)$$

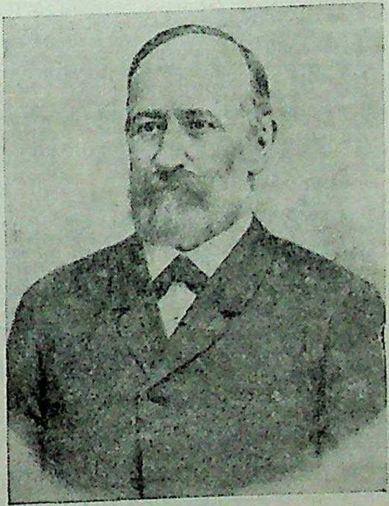
where a is a constant.

Stefan, in 1879, struck by the result of an experiment of Tyndall in which the amounts of heat radiated by a platinum wire at white-heat (1200°C) and at red-heat (525°C) were in the ratio of 11·7, while the ratio of the two temperatures in absolute scale raised to the fourth power, *i.e.*, $(1200 + 273)^4 / (525 + 273)^4$ was also equal to 11·6, suggested the formula

$$R = \sigma T^4 \qquad \ldots (4)$$

where R is the amount of radiation emitted by a body at absolute temperature T and σ is a constant, now known as *Stefan's constant.* On testing the formula by the results of Dulong and Petit, he found that it was well satisfied, so that the formula of Dulong and Petit should be modified as

$$V = k\,(T^4 - T_0^{\,4}) \ldots (5)$$



J. Stefan

where T is the absolute temperature of the hot body and T_0 that of the enclosure.

Since, however, Dulong and Petit did not use a black body in their work, other observers found considerable deviations from the above relation (5) in their researches. But Lummer and Pringsheim using a black body were able to show that Stefan's law was strictly verified for radiations of a black body. In 1884, Boltzmann gave a rigorous theoretical proof of Stefan's law based on thermodynamical principles and showed that the law applies strictly to radiation from a black body. (*Cf*. Ch. VIII). The law is therefore generally known as the *Stefan-Boltzmann law*, which may be enunciated as follows :—

The total amount of heat radiated by a perfectly black body per second per unit area is directly proportional to the fourth power of its absolute temperature,

i.e., $R \propto T^4$ or $R = \sigma T^4$.

This law, which is sometimes called also the *Stefan's fourth power law*, as enunciated above, is not a law of cooling and does not refer to the net loss of heat by a body after exchange with the surroundings. It simply deals with the amount of heat radiated by the body by virtue of its temperature, irrespective of what it receives from the surroundings. Further, it is a *law of total radiation*, applying to the whole range of wavelength, without being limited to any particular wavelength. We shall see below that the distribution of energy in the spectrum of a black body is by no means uniform.

But the law can be extended to represent the net loss of heat by a body after exchange with the surroundings and enunciated as follows :—

If a black body at absolute temperature T is surrounded by another black body at absolute temperature T_0, the amount of heat lost by the former per second per square centimetre is given by

$$R = \sigma (T^4 - T_0^4)$$

Stated thus, it tacitly assumes, in support of Prevost's theory of exchange, that the observed loss of heat is really the difference in the heat radiated by the hot body and that absorbed by it from its surroundings.

Postponing the theoretical proof of the Stefan-Boltzmann law to the chapter on Thermodynamics, we shall here deal only with the following points :—

(*i*) Deduction of Newton's law of cooling from Stefan's law.
(*ii*) Experimental verification of Stefan's law.
(*iii*) Determination of Stefan's constant.

Newton's law deduced from Stefan's law. Considering a hot body at absolute temperature T placed in an encloure at absolute temperature T_0, the rate of loss of heat, according to Stefan's law is given by

$$\begin{aligned} R &= \sigma (T^4 - T_0^4) \\ &= \sigma (T - T_0)(T^3 + T^2T_0 + TT_0^2 + T_0^3) \end{aligned}$$

If the temperature difference $(T - T_0)$ is small, *i.e.*, T nearly equal to T_0, the above expression can be written approximately as

$$\begin{aligned} R &= \sigma (T_1 - T_0) \times 4T_0^3 \\ &= k (T_1 - T_0) \end{aligned}$$

if the enclosure is maintained at constant temperature T_0 ; $k = 4\sigma T_0^3$ (a constant).

This shows that the rate of loss of heat is proportional to the excess of temperature, provided the difference of temperature is small, which is Newton's law of cooling.

Experimental verification of Stefan's law. Lummer and Pringsheim, in 1897, investigated experimentally the total radiation from a black body over a wide range of temperature from 100°C to 1300°C and found Stefan's fourth power law to hold good. The apparatus used by them is shown in Fig. 131.

The black body B employed was of two types according to the range of temperature investigated. For the range 200° and 600°C a hollow copper sphere blackened inside with platinum black and placed in a bath of fused nitrates of sodium and potassium melting at 219°C was used. In the range between 900° and 1300°C an iron cylinder coated inside with platinum black and enclosed in a double-walled gas furnace was employed. The temperature of the bath surrounding the black body could be maintained constant at any

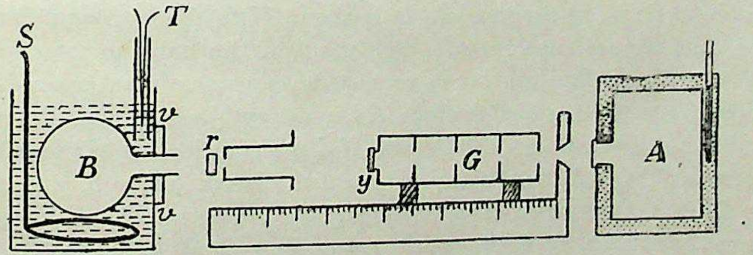


Fig. 131. Apparatus of Lummer and Pringsheim.

desired value. The temperature was measured with a thermocouple T. The opening of B was surrounded by a vessel *vv* through which a current of water circulated in order to protect the instrument used for measuring the radiation from the outside of the hot chamber which served as the black body.

A Lummer and Kurlbaum bolometer G measured the intensity of the emitted radiation. The radiation from B reached the grating of G through a number of water-cooled shutters so that the radiation might be cut off when not required. The bolometer was standardised by means of an auxiliary Féry black body A which consisted of a double walled vessel of sheet copper blackened side, the interspace between the walls containing water which was kept boiling and hence at a constant temperature of 100°C. The bolometer was made to face A and the deflections at various distances from A were noted. It was found that the deflection was inversely proportional to the square of the distance of the grating of the bolometer from the aperture of the black body A. Hence it could be safely assumed that the deflection of the bolometer was proportional to the incident radiation. The bolometer was checked for this condition from time to time during the experiment.

In the actual experiment after heating the bath surrounding B to the desired steady temperature, the water-cooled shutter *r* was opened to allow the radiation from B to fall on the receiving face of the bolometer. When the galvanometer of the bolometer showed a maximum steady deflection, the reading was noted, which was taken as proportional to the incident radiation. With the bath at different constant temperatures, steady deflections of the galvanometer were noted. These data were then reduced to a common arbitrary unit depending on the radiation from the auxiliary black body A at 100°C and kept at a distance of 633 mm. If d is the deflection of the galvanometer, T the absolute temperature of the black body B, and 17°C or 290° K the temperature of the shutter protecting the bolometer, then assuming Stefan's law, $d = a\,(T^4 - 290^4)$. The coefficient a was found to be constant, thereby establishing the truth of Stefan's law.

The constant a however is not the Stefan's constant σ, but some other constant which depends on the calibration of the bolometer, and whose value is found to be $123{\cdot}8 \times 10^{10}$. Kurlbaum was able to estimate the value of σ from the experimental data and found it to be $5{\cdot}32 \times 10^{-5}$ erg per sq. cm. per sec.

More recently Coblentz has checked Stefan's law with greater precision using an electrically heated black body whose temperature is measured by a thermocouple. The amount of radiation emitted by the black body at any given temperature is measured by a special type of *absolute bolometer* devised by Coblentz. It consists of two blackened strips of platinum, suitably arranged so that one of them can be exposed to the radiation, while the other shielded from the radiation can have an electric current passed through it. One junction of a thermocouple is attached to the back of one strip and the other junction to the back of the other strip. Initially, both strips are shielded from radiation and no deflection is observed in the galvanometer connected to the thermocouple. Then one strip is exposed to the radiation and a current is passed through the other, whose strength is such as to keep the galvanometer deflection at zero. This is possible only when the temperature of the two strips remains the same. Hence the electric current is supplying energy to one strip at the same rate as radiation is falling on the other. Measuring the electric energy thus supplied, the amount of radiation falling on the bolometer per second can be readily obtained. Knowing the area of the effective surface of the bolometer, the area of the black body and the distance between the bolometer and the black body, the amount of radiation emitted by the black body per sq. cm. per second can be calculated.

The experimental procedure consists in measuring the difference in the amount of radiation absorbed by the bolometer when it is receiving radiation from the black body at absolute temperature T_1 and when the opening of the enclosure constituting the black body is closed by a water-cooled shutter at absolute temperature T_2. From this E, the difference in energy radiated per sq. cm. per sec. by the black body and the water-cooled shutter can be calculated. Then, if Stefan's law is true,

$$E = \sigma (T_1^4 - T_2^4)$$

Coblentz found that the experimental data satisfied this relation for temperatures up to 1,600°C. Here the value of Stefan's constant σ could be directly estimated and was found to be $5{\cdot}72 \times 10^{-5}$ erg per sq. cm. per sec.

A laboratory method of determining Stefan's constant. The apparatus used is shown in Fig. 132. It consists of a hollow metal hemisphere B, about 10 inches in diameter with its inner surface uniformly blackened, and fitted in a metal box W, which serves as a steam chamber. This arrangement rests on a wooden platform DE with a small hole of about 1 inch in diameter at the centre of the hemisphere. B is heated to a uniform temperature measured by the two thermometers TT inserted in W through which steam is passed. The blackened surface of B with a small hole at its centre constitutes thus the *black body radiator* at a constant temperature T_1°K (that of steam). The heat radiated by it is received by a small silver disc S blackened on the top surface and placed in the central hole. The disc is arranged on the top of an ebonite rod, so that by a special clamping device, it can be put at the centre of the radiating chamber or withdrawn. One junction of a thermocouple is fixed to the bottom face of the disc, while the other is placed in a test-tube containing oil and standing in a beaker C with water. A galvanometer G is introduced in the thermocouple circuit, taking care to keep the wires leading to the terminals of G packed in cotton wool in a vessel A to prevent any disturbing effect due to the difference of temperature in the leads. It may be necessary to include a resistance R in the circuit for suitably adjusting the deflection of the galvanometer.

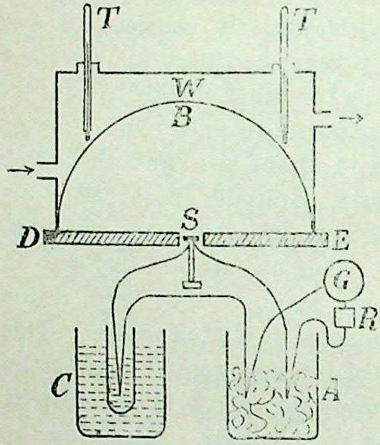


Fig. 132. Stefan's constant apparatus.

When the hemispherical black body is at a constant temperature T_1°K, if the silver disc is introduced in the central hole, it will absorb the radiations emitted by the black body. At any instant, let T_2°K be the temperature of the disc ; the disc, in its turn, will radiate also ; but its rate of absorption will not be the same as its rate of emission. Let R_1 be the amount of radiation *absorbed* by it per unit area per sec., which will be equal to the amount radiated by the black body at T_1°K. Let R_2 be the amount of radiation *emitted* by it per unit area per sec. at the temperature T_2°K. Then by Stefan's law,

$$R_1 = \sigma T_1^4 \text{ and } R_2 = \sigma T_2^4$$

$$R_1 - R_2 = \sigma (T_1^4 - T_2^4) \qquad \dots (1)$$

Since the disc does not emit all the heat it absorbs, it will gain energy, equal to $(R_1 - R_2)$ A, where A is its area. Now, if m is its mass, s its specific heat and $\frac{dT}{dt}$ the rate of change of temperature,

$$m.\,s.\,\frac{dT}{dt} = \frac{(R_1 - R_2)\,A}{J}$$

Substituting for $(R_1 - R_2)$ from (1),

$$m.\,s.\,\frac{dT}{dt} = \frac{\sigma\,A}{J}(T_1^4 - T_2^4)$$

$$\therefore \qquad \sigma = \frac{J\,m\,s}{A(T_1^4 - T_2^4)} \cdot \frac{dT}{dt} \qquad \ldots (2)$$

In this relation (2), m, s and A are constants of the disc which are readily known. J, the mechanical equivalent of heat, is assumed, T_1 is obtained by adding 273 to the temperature of the steam chamber. Hence, if T_2 and $\frac{dT}{dt}$ are determined, σ can be estimated.

The actual experiment consists of two parts :—

(*i*) *Standardisation of the thermocouple*, to measure the temperature difference between the junctions in terms of the deflection of the galvanometer. For this purpose, before passing steam in W, *i.e.*, when B is at the room temperature, the silver disc is arranged at the central hole surrounded by cotton wool. The water bath C is heated and the difference in temperature between it and the disc is recorded on a graph paper against the corresponding deflection of the galvanometer, when a straight line graph is obtained as shown in Fig. 133. From the graph the temperature-difference between the junctions corresponding to 1 cm. deflection in the galvanometer scale is readily got. It is equal to $AB/BC = dT/dx$.

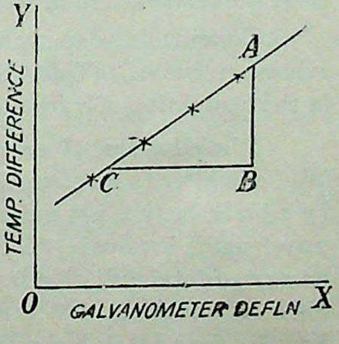


Fig. 133.

(*ii*) *Measurement of dT/dt.* After removing the disc from the hole, steam is passed in W for a pretty long time until B has attained a steady temperature as indicated by the two thermometers. At this stage, the disc is again introduced in the central hole and immediately the deflections of the galvanometer at regular short intervals (2 to 5 secs. at the beginning) are noted. When these data, *i.e.*, time against deflection, are plotted on a graph paper, a curve as shown in Fig. 134 is obtained. A tangent is drawn to the curve at a convenient point P (the curved portion being most suitable). Then DF/EF gives the rate of change of deflection (dx/dt) and using the result of the first part, we get

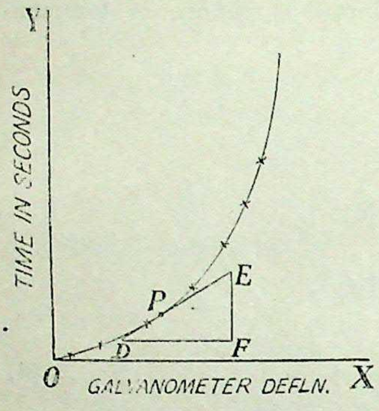


Fig. 134.

$$\frac{d\mathrm{T}}{dt} = \frac{d\mathrm{T}}{dx} \times \frac{dx}{dt} = \frac{\mathrm{AB}}{\mathrm{BC}} \times \frac{\mathrm{DF}}{\mathrm{EF}}$$

Knowing AB/BC and DF/EF, the value of $d\mathrm{T}/dt$ is obtained.

Determination of T_2. From the deflection of the galvanometer, corresponding to the point P chosen for drawing the tangent, we can get the difference in temperature between the junctions from the first graph (Fig. 133). This added to the initial temperature of the disc gives the temperature in °C and adding 273 to it, T_2°K is obtained.

Choosing other convenient points for drawing tangents, an average value of $(d\mathrm{T}/dt)/(\mathrm{T}_1^4 - \mathrm{T}_2^4)$ can be obtained, which is used in the evaluation of σ from relation (2).

Distribution of energy in the spectrum of a black body. We have already mentioned that the intensity of radiation emitted by a black body is not uniformly distributed over the whole range of wavelengths involved. The problem to be solved is to see how the energy of total radiation from a black body is distributed among the different wavelengths at various temperatures, in other words, to find how E_λ for a black body depends on λ and T.

A general solution of the problem is readily obtained from the fact that when the temperature of a body is steadily raised, the colour of the radiation emitted by it changes. Thus, for instance, when a blackened platinum wire is raised in temperature by electrical heating, it begins to appear dull-red at about 525°C, changes to cherry-red at about 900°C, becomes orange-red at 1100°C, yellow at 1250°C and finally white at about 1600°C. This shows that the colour emitted becomes richer in waves of shorter wavelength, in other words, the *maximum intensity of emission shifts towards the shorter wavelength side as the temperature is raised.*

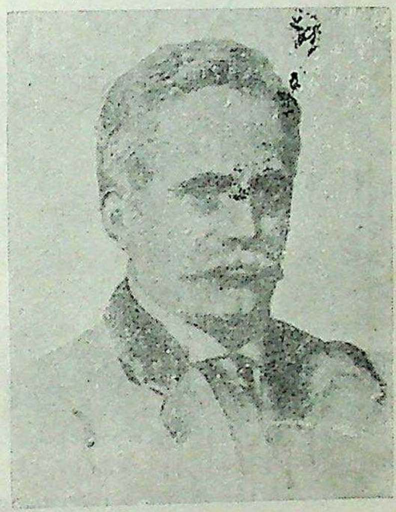
Wien's law of energy distribution. Wien, in 1893, tackled the problem in a more precise and analytical manner, applying the principles of thermodynamics to the black body radiation similar to the method used by Boltzmann in the deduction of Stefan's law and obtained the following two relations :—

$$\lambda_m \mathrm{T} = \text{a constant} \quad \ldots (1)$$

$$\mathrm{E}_m \mathrm{T}^{-5} = \text{a constant} \quad \ldots (2)$$

where λ_m is the wavelength at which the emissive power E_λ is a maximum (E_m) at the absolute temperature T.

The first relation implying an inverse variation of λ_m with T shows that as the temperature increases the maximum intensity of radiation emitted shifts towards shorter wavelengths ; hence it is known as *Wien's displacement law.* The second relation indicates a direct variation of E_m and T^5 and is therefore sometimes called the *fifth power law.*



Prof. Wien

The two relations can be combined into one general relation which is expressed as

$$\mathrm{E} = \mathrm{K}\,\lambda^{-5} f(\lambda \mathrm{T}) \quad \ldots (3)$$

where K is a constant, $f(\lambda\mathrm{T})$ some function of $(\lambda\mathrm{T})$.

Next, making some arbitrary but plausible assumptions concerning the actual mechanism of emission and absorption of radiation Wien obtained the following expression for the energy distribution ;

$$d\mathrm{E} = \mathrm{K}\lambda^{-5}\, e^{-a\lambda/\mathrm{T}}\,.\, d\lambda \quad \ldots (4)$$

where $d\mathrm{E}$ is the amount of energy contained in the spectral region between λ and $\lambda + d\lambda$ emitted by a black body at temperature T, K and a are constants. This expression is known as *Wien's law of energy distribution.*

Experimental study of the black body spectrum. The theoretical predictions of Wien were subjected to a series of experimental tests by Paschen, Lummer, Pringsheim, Rubens and Kurlbaum during the years 1893 to 1899. We shall here describe briefly the *researches of Lummer and Pringsheim* and the results obtained by them. The black body radiation was produced by electrically heating a carbon tube with a small opening; the thermal spectrum was obtained by refraction through a fluorspar prism. A linear bolometer, enclosed in an air-tight case to minimise the absorption due to water vapour and carbon dioxide, was used to measure the radiant energy corresponding to small ranges of wavelength along the spectrum. Corrections were applied to convert the prismatic spectrum into a normal one by means of the known dispersion curve of fluorspar, determined by Paschen. The experiment was repeated for different temperatures of the black body between 620° and 1650°K. The results obtained were represented graphically as shown in Fig. 135, where the amount of energy emitted in a narrow wavelength range was plotted against the mean wavelength of each range. The different curves were obtained for the different temperatures at which the black body was maintained. The total energy of radiation at any one temperature is given by the area between the curve corresponding to that temperature and the horizontal axis. The area is found to increase according to the fourth power of the absolute temperature. Thus Stefan's law is verified. The wavelength corresponding to the maximum energy represented by the peak of the curve shifts to shorter wavelength side as the temperature increases, which confirms Wien's displacement law : $\lambda_m T = $ a constant. Wien's energy distribution formula [relation (4)] is found to agree with the experimental curves for short wavelengths, but not for long wavelengths as was shown by

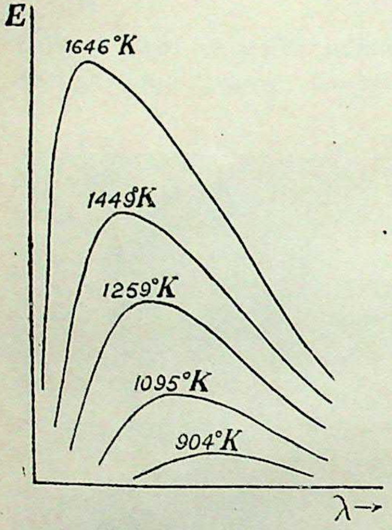
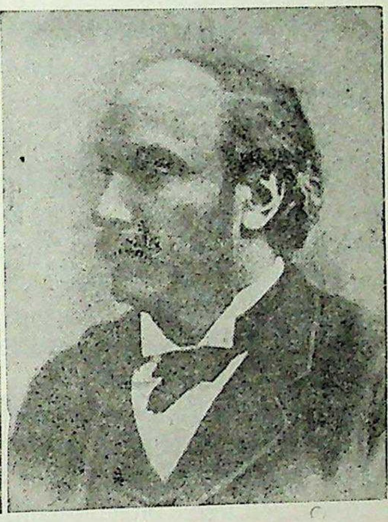


Fig. 135. Energy distribution in the black body spectrum.

Paschen. In order to remove this discrepancy, Rayleigh and Jeans, in 1900, reconsidered the problem of energy distribution in the following different manner.

Rayleigh-Jeans law. According to the electromagnetic theory a black body radiator emits radiations of *continuously variable wavelengths from zero to infinity*. This radiation is imagined as broken up into monochromatic wave trains. Next the number of such wave trains or independent modes of vibration lying within a certain wavelength range, say λ and $\lambda + d\lambda$, is determined by applying the laws of probability. Then the energy carried by each mode of vibration and hence the energy distribution can be obtained. The expression for the energy distribution thus derived is

Sir J. Jeans



Lord Rayleigh

$$dE = B\lambda^{-4}\, Te^{-a/\lambda T}.\, d\lambda \qquad \dots(5)$$

where B and a are constants. This is known as *Rayleigh-Jeans law of energy distribution.*

Rubens and Kurlbaum showed that this formula could be made to fit the experimental curves in the region of long wavelengths, but not of short wavelengths as in the case of Wien's formula.

Planck's law. Both the theoretical laws, of Wien and of Rayleigh Jeans, thus failed to explain experimental results over the entire range of the spectrum, although they were free from error in the application of classical principles. Further, they appeared to lead to wrong and even absurd conclusions. Thus, for instance, in Wien's formula even when $T = \infty$, E is still finite, which is in open contradiction with the experimentally verified Stefan's fourth power law. Likewise, in Rayleigh-Jeans formula, the energy radiated in a given wavelength range $d\lambda$ increases rapidly as λ decreases and approaches infinity for very short wavelengths, which however cannot be true. Moreover, if the expression be integrated over the whole range of wavelengths from zero to infinity on the basis of the classical continuous emission, the total energy thus obtained turns out to be infinite for all temperatures except absolute zero, which is clearly an absurd conclusion.

These almost insurmountable difficulties suggested to Max Planck that after all the fundamental assumptions of the classical theory on which Wien's and Rayleigh-Jeans' laws were based might be at fault. Hence, in 1901, he proposed a new revolutionary hypothesis known as the *quantum theory*, by means of which he was able to derive the correct law of energy distribution in the spectrum of the black body. The line of argument by which he was able to obtain this result may be stated as follows : The classical theory, due to the assumption that the energy-changes of radiators take place continuously has led to inconsistent results. Hence the classical idea of continuous energy changes must be replaced by discontinuous energy-changes, as discrete integral multiples of a small unit of energy, which may be called the *quantum*. The electrical linear oscillators which constitute the radiation of the black body can therefore vibrate only with the integral energy values $0, \varepsilon, 2\varepsilon, 3\varepsilon, \ldots n\varepsilon$, where ε represents the elementary quantum. Further, in order to make theory fit experimental results, it is necessary that ε should be a finite quantity greater than zero and proportional to $1/\lambda$, which means that ε is proportional to ν, the frequency, so that $\varepsilon = h\nu$, where h is a constant of proportionality (now known as *Planck's constant*). Applying the laws of probability to such oscillators, an expression for the energy distribution in the black body spectrum can be obtained, which is of the form

$$dE = \frac{8\pi hc\, \lambda^{-5}\, d\lambda}{e^{hc/k\lambda T} - 1} \qquad \ldots (6)$$

This is known as *Planck's formula of thermal radiation*. It fits the experimental results very well, which argues to its correctness. Furthermore, Wiens and Rayleigh-Jeans' formulae can be deduced from it as special cases holding good under certain assumptions.

The quantum theory, thus introduced by Planck, has revolutionised classical ideas and forms one of the fundamental concepts of Modern Physics. We have already seen how Einstein was able to apply it successfully to the problem of specific heats. It has also been employed to explain various other phenomena, such as photo-electric effect, Compton effect, atomic structure and origin of spectral lines, etc. which are dealt with in the course on Modern Physics.

PRACTICAL APPLICATIONS OF THERMAL RADIATION

1. Measurement of high temperatures—Radiation pyrometry. The art of measuring high temperatures is called *pyrometry* and the instruments used for the purpose *pyrometers.* We have already seen that gas, resistance and thermoelectric thermometers can be employed to measure high temperatures upto a certain limit (*Cf.* Chapter I). Thermal radiation also can be used to measure high temperatures, since, as we have seen in the preceding pages, the radiation from a black body depends solely on its temperature. Such a device is known as *radiation pyrometry* and the apparatus used *radiation pyrometers.*

The *superiority of the radiation pyrometers* over the other pyrometers lies in the fact that they can be employed to measure any temperature, however high it may be, and wherever the object may be. In the other pyrometers, the measuring instrument has to be placed in contact with the hot body so that it may acquire the temperature of the body. This imposes an upper limit depending on the melting point of the material of the instrument, which, in practice, is about 1600°C. But in the case of the radiation pyrometers, there is no such upper limit, since the instrument itself need not be placed in contact with the hot body nor raised to the temperature of the body. Further, no extrapolation is required in estimating very high temperatures, as the radiation formulae on which these pyrometers are based are found to be valid at all temperatures.

The radiation pyrometers, however, suffer from two drawbacks. (*i*) Since they are based on laws that govern strictly black body radiation alone, when they are employed to measure the temperature of any hot body, they give that temperature at which a perfectly black body would have the same intensity of emission as the body whose temperature is being measured. The temperature thus actually measured is the *black body temperature* of the source, which is evidently less than its actual temperature, since, all other conditions being the same, the radiation from a black body is the most intense. Hence the greater the departure of the body from perfect blackness, the greater will be the error in the estimation of its temperature. (*ii*) There is a lower practical limit, about 600°C, below which radiation pyrometers cannot be used for accurate measurement, since the emission from bodies becomes too small to be estimated correctly at lower temperatures.

Radiation pyrometers in use. In measuring high temperatures by means of radiation, two types of instruments are used :—

(*i*) *Total radiation pyrometers*, which measure the total radiation emitted by the source, the temperature being then deduced by the application of Stefan's law.

(*ii*) *Optical* or *spectral pyrometers*, which compare the intensity of radiation emitted by the source, in a particular portion of the spectrum, with the intensity of emission of the same wavelength from a standard lamp to secure conditions of equal brightness, the temperature being then deduced by making use of Planck's law.

The optical pyrometers can be further classified under two heads according to the different techniques used for the comparison :—

(*a*) *the disappearing filament type*, where the standard light is varied until it is equal to the intensity of the source ;

(*b*) *the polarising type*, where the standard light is kept constant and the radiation from the source is varied by means of a polarising device until it is equal in intensity to the standard.

We shall now give a brief description of these three kinds of pyrometers.

Total radiation pyrometer. Féry was the first to device this type of pyrometer, which is therefore ordinarily known as Féry's pyrometer. A modern version of this pyrometer is shown in Fig. 136. It consists of a concave mirror M made of copper and nickelled in the front surface, having a small opening in the centre, into which an eyepiece E is fitted. In front of M a small diaphragm D is mounted and immediately behind it a metal-

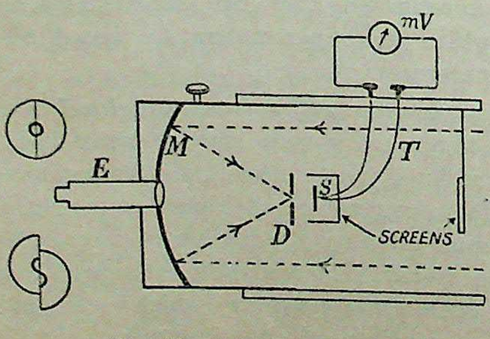


Fig. 136. Féry's pyrometer.

lic strip S is arranged. The front surface of S facing D is blackened, while to its back surface one junction of a thermocouple T is fixed. The other junction of T as well as S are protected from the direct radiations by suitable screens. The leads from the thermocouple are connected to a millivoltmeter mV which measures the e.m.f. developed when the radiation from the source whose temperature is to be measured, after being focused by M, falls on the receiver S through D. The mirror M can be moved forwards and backwards for the purpose of focusing the radiations on S.

In order to obtain accurate focusing the following device is employed. The diaphragm D is constituted by two semi-circular mirrors inclined to each other at an angle of about 5° with a central hole of about 1·5 mm. to allow the incident radiation to pass. When this diaphragm is viewed through the eye-piece E, if the focusing is perfect, the images of the two halves of the diaphragm coincide to form a complete circle ; but if the focusing is not accurate, the two halves will not coincide but appear displaced as shown in the figure. The concave mirror M is moved till this relative displacement of the two halves disappears.

In the actual use of the apparatus, arrangements must be made, so that the image of the source formed by the concave mirror is slightly larger than the aperture of the diaphragm, in which case the thermocouple measures the intensity of the image and not the total radiation and hence the reading of the pyrometer becomes independent of its distance from the source. For if the distance of the source is doubled, the amount of radiation falling on the concave mirror is reduced to one-fourth according to the inverse square law, but as the area of the image is at the same time reduced to one-fourth, the intensity of the image remains unaltered, provided the image is larger than the aperture. When the source is at a given distance, the size of the aperture through which radiations issue from the source must be large enough in order that its image is always bigger than the diaphragm aperture, and can be calculated from the geometry of the apparatus.

In making a measurement, if V is the reading indicated by the millivoltmeter, then

$$V = a\,(T^b - T_0^{\,b})$$

where T is the black body temperature of the source, T_0 the temperature of the receiver S, which can be generally neglected in comparison with T, a constant of proportionality and b another constant which, though it must be equal to 4 according to Stefan's fourth power law, varies from 3·8 to 4·2, depending upon the instrument, due to various causes, such as the e.m.f. generated being not exactly proportional to the difference of temperature between the two junctions, conduction effect along the leads of the thermocouple, spurious effects produced by stray and diffuse reflections, etc.

Because of this actual deviation from the fourth power law, the pyrometer has to be calibrated by using radiations from a black body at different temperatures which can be accurately measured by a standard thermocouple. In this way, the millivoltmeter can be calibrated directly in degrees or a calibration curve can be drawn connecting the reading of the millivoltmeter and temperature. Such a directly calibrated instrument is, however, useful only within the range of calibration, which naturally limits the extent of its utility.

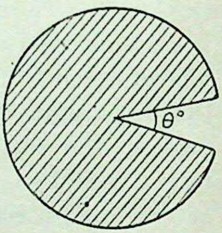


Fig. 137.

But this drawback has been overcome by a *rotating sector device*, which enables the instrument to measure even very high temperatures. An opaque disc, from which a sector making an angle θ at the centre is cut off, as shown in Fig. 137, is rotated about the axis of the pyrometer tube in the path of the incident radiation, so that only a fraction of the radiation enters the pyrometer per revolution. If T_1 is the temperature, now measured by the instrument, then the actual temperature T of the source, according to Stefan's law, is given by

$$\frac{T_1^4}{T^4} = \frac{\theta}{360}$$

$$\therefore \qquad T = T_1 \left(\frac{360}{\theta}\right)^{\frac{1}{4}}$$

Supposing that $\theta = 22·5°$ and $T_1 = 1800°K$,

$$T = 1800 \left(\frac{360}{22·5}\right)^{\frac{1}{4}} = 1800\ (16)^{\frac{1}{4}}$$

$$= 1800 \times 2 = 3600°K.$$

Disappearing filament optical pyrometer. This type of pyrometer was first introduced by Morse and later improved by Holborn and Kurlbaum, Henning and others. It consists essentially of a telescope where the cross-wire is replaced by the filament of an electric lamp L, as shown in Fig. 138. There are two diaphragms DD, one on each side of L. The filament of the lamp can be heated to different high temperatures by adjusting the current in the battery circuit feeding the lamp by means of the rheostat R, the current itself being measured with the help of a sensitive ammeter A.

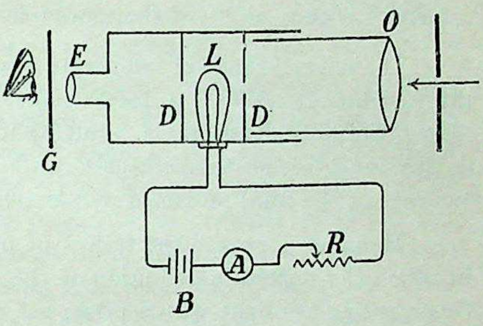


Fig. 138. Disappearing filament pyrometer.

By suitably adjusting the position of the objective O, radiation from the source, whose temperature is to be measured, is focused on the lamp where a heat image is formed. The lamp is viewed through the eye-piece E in front of which a red glass filter G is placed. Current is passed through the lamp and its strength varied until the filament becomes invisible against the image of the source. If the current is too strong, the filament will appear brighter than the image ; if the current is too weak the filament will appear dark in contrast to the image. The red glass helps the eye to obtain the matching for approximately monochromatic radiation as it allows only a narrow band of wavelength to pass through.

When the matching is thus secured by the condition of the disappearing filament against the background of the image of the source, the temperature of the filament is the same as that of the source according to Planck's law, since the brightness or energy emitted per sq. cm. per second is the same in the two cases.

From the value of the current I feeding the lamp under these conditions, the temperature T of the filament and hence of the source can be calculated using the relation

$$I = a + bT + cT^2$$

where T is in the absolute scale, and a, b and c are constants which can be determined by calibrating the instrument with three known temperatures. In practice, however, it is much more convenient to calibrate the ammeter to read directly in degrees by using the instrument with a black body raised to different known temperatures, measured with a standard thermocouple.

The normal range of temperature which can be measured with this instrument is 600°C to 1500°C, since beyond this upper limit the filament rapidly deteriorates. But by the use of a rotating sector device, much higher temperatures can be measured, as explained in the case of the total radiation pyrometer.

Henning improved the technique into a real spectral pyrometer, in which the uncertain definition of the wavelength is removed by decomposing the light with a prism before it reaches the eye, so that matching could be done for a very short interval $d\lambda$ of the wavelength. But, on account of the spectral decomposition, Henning's pyrometer has less light gathering power and cannot be used below 1000°C.

Polarising optical pyrometer. Wanner constructed an optical pyrometer where the ray of a particular colour from the source is compared with a ray of the same colour from a standard electric lamp with the help of a polariser. The essential parts of this instrument are shown in Fig. 139. Radiation from the source and the comparison light from the electric lamp L, the latter after being deviated through 90° by a right-angled prism P, enter the apparatus through two circular holes C and D which are symmetrically situated about the optic axis of the system. Both the beams are rendered parallel by means of an achromatic lens L_1 placed at a distance from the holes equal to its focal length. The parallel beams are then dispersed by a direct vision spectroscope S and pass through a polarising Rochon prism R, which divides each beam into two beams polarised in orthogonal planes. These polarised beams limited by a slit D_1 pass through a biprism B placed in contact with a second achromatic lens L_2 which focuses the beams on a second slit D_2. The biprism produces in the two beams deviations of such

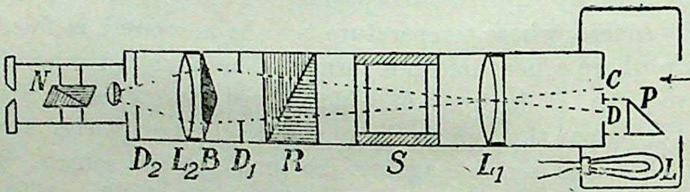


Fig. 139. Wanner's polarising type pyrometer.

amount that the images from the two sources are brought into juxtaposition. These images are circular since the holes C and D are circular, but the biprism splits them into semi-circles. Six out of the eight polarised images are stopped and only the remaining two are observed through the analysing nicol N.

If the two beams are of equal intensity, a uniformly illuminated circular image with a diametrical line will be observed when the plane of polarisation of N makes an angle of 45° with the plane of polarisation of each component. When the nicol is rotated in either direction from this position, the brightness of one-half of the circle increases while that of the other half diminishes. If the two beams are of unequal intensity, matching is obtained by rotating the nicol in either direction to get the uniformly illuminated circular image. The angle through which the nicol is rotated to obtain this result can be found with the help of a graduated circular disc attached to the nicol. If θ is the angle thus measured when radiation from a source at absolute temperature T is matched with the light from the standard lamp, then it can be shown that

$$\log \tan \theta = a + \frac{b}{T},$$

where a and b are constants.

By determining two values of θ corresponding to two known values of T, a straight line graph can be drawn, from which the temperature for any value of θ can be obtained. In practice, however, the instrument is calibrated by direct comparison with a standard thermometer and the disc attached to the nicol is directly graduated in degrees.

It may be noted that the method of direct calibration of the different radiation pyrometers restricts their range of utility to a much greater extent than in the case of the gas, resistance and thermo-electric pyrometers. All the same, they are preferred in industry, since they are quicker in indication, easier to use and need not be put in contact with the body whose temperature is to be measured.

2. Solar radiation. The sun, which is the centre of the solar system composed of several planets, our earth being one of them, is the source of thermal energy, without which life would be impossible on earth. It emits continuously radiant energy in space, of which only an insignificant part reaches the earth. But even of this small incident radiation, a good part is lost by reflection and absorption in the earth's atmosphere. Water vapour, snow, cloud and dust particles in the atmosphere act as scattering agents and send back the solar radiation into space again. The amount of radiation absorbed is also great, varying from 20 to 40% depending on the time of the day and the season of the year.

From a measurement of even this very small amount of radiant energy received by the earth from the sun, it is possible to estimate the *temperature of the sun* by the application of laws that govern thermal radiation. For this purpose it has been found necessary to determine first a constant defining the rate at which solar radiation is received by the earth and known as the *solar constant*. We shall therefore describe first the methods by which the solar constant has been determined and then show how the temperature of the sun can be estimated from a knowledge of the solar constant.

Solar constant is defined as *the amount of solar radiation received per minute by one sq. cm. of a perfectly black surface placed at the mean distance of the earth just beyond the earth's atmosphere, and at right angles to the direction of the sun's rays, at noon on the mean solar day.*

The solar constant is determined by instruments devised for that purpose, called **pyrheliometers.** There exist different types of pyrheliometers, all working however on the same basic principle.

(*a*) **Water-flow pyrheliometer**, shown in Fig. 140, consists of a cylindrical double-walled vessel V terminating in a conical shape at one end and blackened on the inside. A manganin coil MM, through which current may be passed from outside, is wound over the conical part. The cylindrical vessel which constitutes the absorption chamber is surrounded by a Dewar flask D. Water is circulated steadily in the space between the walls of V, using a spiral SS for good contact on

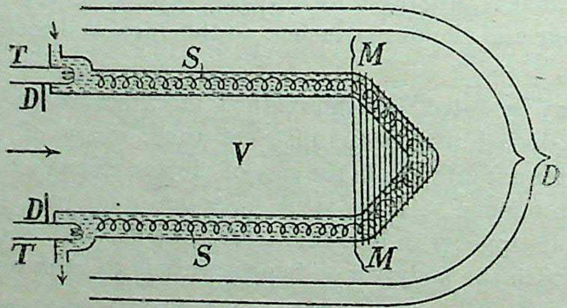


Fig. 140. Water-flow pyrheliometer.

the walls. Solar radiation is admitted into V through the open end, after being restricted in width by a polished diaphragm DD. The radiation will be absorbed completely by the blackened inner surface of V and the heat will be communicated to the circulating water. After letting in the radiation for a known time, the temperatures of the inflowing and outflowing water are noted with two platinum-resistance thermometers TT. The radiation is then screened off and the same conditions are reproduced by passing through the manganin coil a suitable current I under a potential difference E, both of which can be measured with an ammeter and voltmeter introduced in the electric circuit. The quantity of heat received by V from solar radiation is given by EI/J cal./sec. Knowing the area of the blackened surface of V, the solar constant can be calculated, as indicated below.

(*b*) **Water-stir pyrheliometer,** used in the Astrophysical Observatory, Washington, U.S.A. is shown in Fig. 141. The absorption chamber V, blackened inside, with its rear end conical in shape is surrounded by water contained in a calorimeter CC which is stirred vigorously by a special stirring arrangement S run by a motor from outside. Solar radiation is admitted into V through a diaphgram D of known aperture. The chamber absorbs completely the incident radiation producing a rise in temperature of the water in the calorimeter, which is measured by a platinum resistance thermometer PP, whose wire is carefully wound upon an insulating frame round V. A mercury thermometer T is also inserted in the calorimeter. The calorimeter is carefully protected from air currents and thermal effects from outside. To find the amount of heat absorbed by V from solar radiation, after screening off the solar radiation, identical conditions are reproduced by supplying a known amount of electrical energy to the manganin coil MM wound on the chamber.

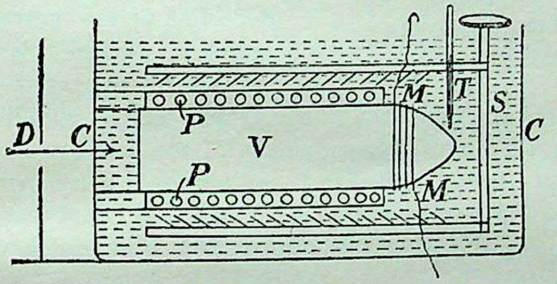


Fig. 141. Water-stir pyrheliometer.

(c) **Angström's pyrheliometer.** Angström used a much simpler form of pyrheliometer shown in Fig. 142. It consists of two thin exactly similar blackened strips of platinum or manganin, A and B, suitably mounted so that one can be exposed to solar radiation falling normally on it and the other can be shielded by a screen S and electrically heated. A pair of copper constantan thermo-junctions are fixed to the backs of A and B. As the exposed strip A gains solar energy, the galvanometer G in the thermocouple circuit shows a deflection. Current is now passed through B and its strength adjusted until the deflection of the galvanometer is annulled. When this condition is realised the temperature of A and B is the same and hence the rate at which heat is supplied to both is the same. From the known values of the current and potential difference, the heat supplied to B and hence the solar energy absorbed by A can be readily obtained. It may be noted that Coblentz's absolute bolometer described on p. 305 is a modification of this pyrheliometer.

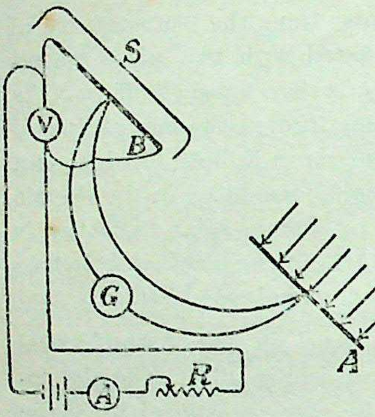


Fig. 142. Angstrom's pyrheliometer.

Estimation of the solar constant. Having thus determined the energy absorbed by a known area by any one of the above instruments and making correction for absorption by the earth's atmosphere, the solar constant can be calculated as follows :

To eliminate the effect of absorption by the atmosphere, the value the solar constant is found for different elevations of the sun on the same day under constant sky conditions. If S is thus the observed value of the solar constant, the true value of the solar constant, S_0, can be shown to be given by the relation

$$S = S_0 \, a^{\sec z}$$

where a is called the transmission coefficient, which varies from 0·55 to 0·85, and Z the zenith distance of the angular altitude of the sun.

Taking logarithms,

$$\log S = \log S_0 + \sec Z \log a.$$

From the experimental data, if a graph is plotted taking log S along the Y-axis and sec Z along the X-axis, it will be a straight line, whose intercept on the Y-axis will give log S_0, from which S_0 can be found. The results of observations vary a good deal. The most reliable values so far obtained lie between 1·9 and 2·6 calories per sq. cm. per minute.

Temperature of the sun. The sun consists of a central hot core surrounded by a thick shell which is known as the *photosphere.* Here we are concerned only with the *temperature of the photosphere.* The temperature inside the central core is very much greater, having the tremendous value, of 20,000,000°K at the centre as deduced from the surface temperature and the heat conductivities of the gases constituting the material of the sun. Further, we here calculate the *effective temperature, i.e.*, the temperature which must be assigned to the photosphere of the sun in order that its total radiation should have its actual value on the assumption that it radiates as a black body. This black body temperature of the sun can be estimated from the known value of the solar constant as follows :

Let R be the amount of radiation emitted per sec. by 1 sq. cm. of the sun's surface. If a is the radius of the sun, the total amount of radiant energy emitted by the sun per minute $= 4\pi a^2 \times R \times 60$.

This energy is received by a sphere whose radius is equal to that of the earth's orbit.

If b is the radius of the earth's orbit, the total amount of radiant energy received by the surface of a sphere of radius b per minute $=$ $4\pi b^2 \times S$, where S is the solar constant.

$$\therefore \quad 4\pi a^2 \times R \times 60 = 4\pi b^2 \times S$$

Or
$$R = \left(\frac{b}{a}\right)^2 \times \frac{S}{60}$$

According to Stefan's law $R = \sigma T^4$

where T is the absolute temperature of the sun.

$$\text{Hence } T = \left(\frac{R}{\sigma}\right)^{\frac{1}{4}} = \left\{\frac{b^2}{a^2} \cdot \frac{S}{60} \cdot \frac{1}{\sigma}\right\}^{\frac{1}{4}}$$

Given $S = 1{\cdot}937$ cals. per sq. cm. per minute

$\sigma = 1{\cdot}37 \times 10^{-12}$ cals. per sq. cm. per sec.

$a = 4{\cdot}3 \times 10^5$ miles

$b = 9{\cdot}28 \times 10^7$ miles

$$T = \left\{ \left(\frac{9{\cdot}28 \times 10^7}{4{\cdot}3 \times 10^5} \right)^2 \times \frac{1{\cdot}937}{60} \times \frac{1}{1{\cdot}37 \times 10^{-12}} \right\}^{\frac{1}{4}}$$

$$= 5780^\circ\text{K}$$

Note : (*i*) The temperature of the sun may also be estimated using Wien's displacement law.

$$\lambda_m T = \text{constant} = {\cdot}293$$

Abbot's investigation shows that $\lambda_m = 4753$ A.U.

$$T = \frac{{\cdot}293}{4753 \times 10^{-8}} = 6060^\circ\text{K}.$$

This temperature, sometimes called the *colour temperature*, is nearly 300° higher than that deduced from total radiation. This discrepancy can be explained by the fact that, contrary to the assumption made, the sun does not actually radiate like a black body.

(*ii*) **Temperature of stars.** The stars may be considered as so many suns, which are however at enormously greater distances than the sun. The methods employed to determine their temperatures are almost the same as those used in the case of the sun. It is to be noted, however, that since the diameters of stars are not known in many cases, application of Stefan's law of total radiation is ordinarily not possible ; the temperatures are usually deduced from the distribution of intensity in their emission spectra, making use of Wien's displacement law. The temperatures of stars vary from 2800°K (red stars) to 30,000°K (bluish white stars). The values evidently refer to the surface temperature, while that in the interior will be several millions of degrees, as in the case of the sun.

(*iii*) **Source of solar energy.** The fact, that although the sun is constantly radiating energy at the rate of 3 S × 10^{33} ergs per sec. yet its temperature is sensibly constant, has given rise to the interesting but difficult problem concerning the source of solar energy. What is the mechanism by which the sun is making up for the enormous loss of energy by radiation ? Only recently, thanks to intense researches in artificial transmutations of nuclei, a plausible explanation has been proposed, which is known as *thermonuclear origin of solar energy*. The release of the enormous amount of energy is due to thermonuclear interactions of the *fusion* type, caused by the very high temperature (20,000,000°C) in the interior, in which four hydrogen nuclei or protons fuse together to form a helium nucleus by the so-called "*proton-proton*" or "*carbon-nitrogen*" *cycle* closed chain reactions. In such processes certain amount of mass disappears, which according to Einstein's mass-energy relation, corresponds to a tremendous amount of energy, which is released. Thus, for instance, when four protons combine to form a helium nucleus, 0·0287 unit of mass disappears, and the corresponding energy released is roughly 26×10^{18} ergs. Considerations of the actual hydrogen and helium content of the sun show that the amount of energy involved in the above stated nuclear processes is enough to keep the sun going at its present internal temperature for about 30 billion years. Assuming that the sun must have been formed not much before the formation of our earth, the age of the sun must be more or less the same as that of the earth, about 3 to 4 billion years. Hence the sun must be considered still young and will continue to shine with approximately the present intensity for billions of years to come. The same explanation has been extended to the origin of stellar energy.

3. Infra-red photography. Glass, which is ordinarily used as the base in photographic plates, is transparent to light while opaque to thermal infra-red radiation. But in recent years great progress has been made in the manufacture of special kinds of glass which are transparent only to the infra-red region of the spectrum. Such glasses, used in the preparation of photographic plates, have made it possible to obtain long distance photographs, even under misty conditions using infra-red radiation.

4. Some everyday applications. The fact that good reflectors are bad absorbers and bad radiators is utilised in making firemen helmets and metallic tea-pots highly polished on the outside. Since glass absorbs almost completely thermal radiation, it finds application in glass green-houses, glass fire-screens, etc. Similarly water absorbs almost 90% of heat radiation, which shows the importance of the presence of water vapour in the atmosphere, protecting the earth from the more intense heat rays of the sun during the day and from extreme cold during the night; in very dry districts on the contrary, where there is little water vapour in the air, the days are intensely hot and the nights extremely cold. Gases are poor radiators of heat, hence in the construction of furnaces, the gases are made to fall on fire-bricks, which radiate heat freely. Because black bodies are the best absorbers of radiant heat, a black dress is uncomfortable during the hot summer, while a white one is cool.

QUESTIONS

1. Distinguish between thermal conductivity and thermometric conductivity. Bring out the connection between the two. Describe the Searle's method of determining the thermal conductivity of a solid.

(*Madras University ; Punjab University 1950*)

2. Show that in the steady state of a metal bar heated at one end

$$\frac{d^2\theta}{dx^2} = \mu^2\theta$$

where the symbols have the usual significance.

Hence prove that the length to which the wax melts in the steady state along a wax coated bar is proportional to the square root of the coefficient of thermal conductivity of the material of the bar.

(*Allahabad University 1955 ; Madras University*)

3. Describe Ingen-Hausz's experiment and prove from the mathematical theory that the conductivities of the different bars vary as the square of the length up to which wax is melted. (*Allahabad University 1950*)

4. Describe fully Forbes' method of determining the thermal conductivity of a metallic bar. Develop the formulae used.

(*Punjab University 1957, 1955, 1954 ; Utkal University 1953 ; Allahabad University 1951 ; Lucknow University 1950 ; Madras University*)

5. Define coefficient of thermal conductivity and describe Lees' method for determining the thermal conductivity of metals.

Equal bars of copper and aluminium are welded end to end and lagged. If the free ends of copper and aluminium are maintained at 100°C and 0°C respectively, find the temperature of the welded interface. Assume the thermal conductivity of copper and aluminium to be 0·92 and 0·50 respectively. **Ans.** 64·8°C. (*Punjab University 1953, 1956, 1960*)

6. Describe Lees' method of determining the thermal condutivity of a bad conductor. (*Bombay University 1947; Madras University ; Tripos Part I*)

7. Define thermal conductivity and explain how the conductivities of (*a*) good conductors, (*b*) bad conductors may be measused. (*Tripos Part I*)

8. If the thermal conductivity of ice = 0·005, its latent heat = 80 cals./gm. and density at 0°C = 0·91, find the time in which a layer of ice 3 cms. thick on the surface of a pond will increase in thickness by 1 mm. when the temperature of the surrounding air is 20°C below zero. **Ans.** 3 mins. 38·4 secs.

(*Madras University*)

9. Distinguish between thermal conductivity and thermometric conductivity of a substance. Describe a method of finding the thermal conductivity of a solid.

Calculate the rate of increment of the thickness of ice layer on a lake when the thickness of ice is 20 cms. and the air temperature is -40°C. Thermal conductivity of ice = 0·004 cal./cm.$^{-1}$ sec.$^{-1}$, °C^{-1}, density of ice = 0·92 gm./c.c. and its latent heat = 80 cals. gm. After what time the thickness will be doubled ? **Ans.** Rate of increment = 1/9200 cm./sec. Time for the thickness to be doubled = 76 hrs. 40 mins.

(*Bihar University 1954*)

10. In an experiment performed to find the thermal conductivity of cardboard by Lees' method, the following observations are made :

Steady temperature of upper disc = 99·5°C

Steady temperature of lower disc = 83·5°C

Time taken for the upper disc to cool from 86° to 81°C = 4 mins.

Thickness of cardboard disc = 4·8 mm.

Thickness of upper disc = 1 cm.

Material of upper disc is copper. Find the thermal conductivity of card board. **Ans.** 0·000566. (*Madras University*)

11. What is meant by the coefficient of thermal conductivity of a substance ?

Calculate approximately the heat passing per hour through the walls and windows of a room 5 by 5 metres, if the walls are of bricks of thickness 30 cms. and have windows of glass 3 mm. thick and total area 5 sq. metres. The temperature of the room is 30°C below that of the outside and the thermal conductivities of bricks and of glass are 12×10^{-4} and 25×10^{-4} c.g.s. units respectively. **Ans.** $4{\cdot}91 \times 10^7$ calories. (*Allahabad University 1954*)

12. In one of Searle's experiments to determine K, the readings of the thermometers inserted in the holes at a distance of 5 cm. from each other are 80°C and 70°C. If a litre of water flows through the coil in 7 mins. and the radius of the bar is 2 cms., calculate the thermal conductivity of the bar. Inflow temp. = 30°C ; outflow temp. = 40°C. **Ans.** 0·947. (*Madras University*)

13. Describe and explain the cylindrical shell method of determining the conductivity of a solid. (*Bombay University 1948*)

14. A steady stream of water flowing at the rate of 500 gms. a minute through a glass tube 30 cms. long, 1 cm. in external diameter and 8 mm. in bore, the outside of which is surrounded by steam at a pressure of 760 mm. of mercury, is raised in temperature from 20°C to 30°C as it passes through the tube. Find the thermal conductivity of glass. **Ans.** 0·001315 c.g s. units. (*Patna University 1948*)

15. A furnace has walls of asbestos of thickness 1 cm. A short cylindrical box of circular section and of radius 5 cms. is fixed with one face outside the furnace wall. A steady steam of water is passed through the chamber at the rate of 300 c.c. per min. The temperature of the water entering the chamber is 17°C and of the water leaving is 23°C. If the conductivity of asbestos is 0·0004, what is the inner temperature of the furnace ? **Ans.** 975°C. (*Madras University*)

16. Define conductivity. Deduce expression for the flow of heat in a long bar when it has acquired a steady state. (*Banaras University*)

17. The interior of an iron steam-pipe, 2·5 cm. internal radius, carries steam at 140°C and the thickness of the wall of the pipe is 3 mm. The coefficient of emission of the exterior surface (heat lost per sec. per sq. cm. per degree excess) is 0·0003 and the temperature of the external air is 20°C. If the thermal conductivity of iron is 0·17 c.g.s. unit, find the temperature of the exterior surface and also how much steam is condensed per hour per metre length of tube, the latent heat of steam at 140°C being 509. **Ans.** 139·94°C., 448 gms. (*London B. Sc.*)

18. Describe and give the theory of a method useful for a practical determination of the thermal conductivity of a liquid. (*London B. Sc.*)

19. Discuss the difficulties which beset the investigation of the thermal conductivity of gases and indicate how and to what extent they have been overcome ? (*London B. Sc.*)

20. Steam at 100°C is passed through a rubber tube, 14·6 cms. length of which is immersed in a copper calorimeter of thermal capacity 23 cals., containing 440 gms. of water. The temperature of the water and calorimeter is found to rise at the rate of 0·019°C every second when they are at the room temperature (22°C). The external and internal diameters of the tube, are 1 cm. and 0·75 cm. respectively. Calculate the conductivity of rubber. **Ans.** 0·000354.

21. Distinguish between natural and forced convection, and give examples to illustrate the part played by convection in atmospheric phenomena.

22. Discuss the validity of Newton's law of cooling. How is this law distinguished from the Stefan's law of radiation ? Show that Newton's law follows algebraically from Stefan's law for small temperature differences between a body and its surroundings.

23. Write notes on :—

(*i*) Convective equilibrium of the atmosphere. (*Delhi University 1955*)

(*ii*) Central heating of buildings.

24. State and explain the law of cooling of Stefan and show how it is an improvement on the other laws of cooling. (*Madras University*)

25. What is a black body ? What are the characteristics of a black body radiation. How has it been realised in practice ? Describe how Stefan's law has been verified with it ? (*Allahabad University 1949* ; *Madras University* ; (*Punjab University 1961*)

26. How can you show that the radiation from an enclosure depends only on the temperature and not on the material of its walls.

Describe a radiation pyrometer. (*Delhi University 1955*)

27. Show that the radiation in a uniform temperature enclosure depends only on the temperature of the enclosure and not on the material of which it is made or on the presence of any other bodies in the enclosure. Why is such radiation called "full radiation" and why is it the same as "black body radiation".

28. Describe a sensitive instrument for the detection and measurement of radiant heat.

Explain how the reading on such an instrument depends on the area, distance, inclination and temperature of a black surface, the radiation from this being received by the receiving surface in a direction normal to that surface. (*Tripos Part I*)

29. What are the principal points of resemblance and difference between radiant heat and visible light ? How would you demonstrate them experimentally. (*Oxford and Cambridge*)

30. Explain the terms 'emissive power' and 'absorptive power'. Deduce that at any temperature the ratio of emissive power to the absorptive power of

a substance is constant and is equal to the emissive power of a perfectly black body. (*Baroda University 1951*)

31. Explain Kirchhoff's law concerning the relation between the absorptive and emissive powers of a body ? Discuss some of the important applications. (*Madras University*)

32. Discuss the evidence both theoretical and experimental showing that good emitters are good absorbers. (*Punjab University 1953*)

33. State and explain the laws relating to the radiation and temperature of a radiating body. What do you mean by (*a*) perfectly black body, (*b*) coefficient of absorption, (*c*) coefficient of emission. (*Madras University*)

34. State Newton's law of cooling mentioning its limitations. How would you verify it experimentally ?

A body initially at 80°C cools to 64°C in 5 mins. and to 52°C in 20 mins. What will be its temperature after 15 mins. and what is the temperature of its surroundings ? **Ans.** 43°C ; 16°C.
(*Patna University 1951 ; Punjab University 1951, 1952*)

35. Explain what you understand by a black body. State Stefan's law of radiation and prove it from thermodynamical consideration. Indicate how it can be verified. (*Punjab University 1949, 1950 ; Roorkee University, 1951, 1959*)

36. State and explain Stefan's law. Describe an experiment to verify the law.

Luminosity of Rigel star in Orion constellation is 17,000 times that of our sun. If the surface temperature of the sun is 6000°A, calculate the temperature of the star. **Ans.** 68520°K. (*Punjab University 1959*)

37. Discuss fully the methods that have been used to measure high temperature in the neighbourhood of 2000°C. (*Madras University*)

38. Describe the radiation method of measuring high temperatures. (*Delhi University 1951*)

39. Define solar constant. Explain with necessary theory how the solar constant is determined. How is the temperature of the sun estimated from the data of the solar constant ?
(*Allahabad University 1953 ; Punjab University 1952 ; Nagpur University 1953*)

40. Describe an experiment by which the solar constant is determined. Calculate the effective temperature of the sun from the following data : Solar constant = 2·279 cal./sq. cm./min. radius of the sun = $4 \cdot 3 \times 10^5$ miles, distance of the sun from the earth = $9 \cdot 3 \times 10^7$ miles, Stefan's constant = $1 \cdot 37 \times 10^{-12}$ cal./sq. cm./sec. **Ans.** 6001°K. (*Madras University*)

41. Write short notes on :—

(*i*) Provost's theory of exchange. (*Punjab University 1951*)
(*ii*) Black body radiation. (*Delhi University 1956*)

(*iii*) Perfect black body and its actual realisation. (*Delhi University 1952*)

(*iv*) Stefan's law. (*Delhi University 1955*)

(*v*) Solar constant. (*Delhi University 1956*)

(*vi*) Determination of temperature of the sun. (*Delhi University 1952*)

(*vii*) Optical pyrometers. (*Allahabad University*)

(*viii*) Boys' radiomicrometer. (*London B.Sc.*)

(*ix*) Infra-red region of the spectrum. (*Cambridge*)

(*x*) Origin of solar energy.

CHAPTER VI

THE NATURE OF HEAT

CALORIC, DYNAMIC AND KINETIC THEORIES

Introduction. In the foregoing chapters we have collected a considerable amount of experimental facts concerning the properties and effects of heat, along with several associated phenomena; we have even tried to understand them by some plausible explanations, though partial and disconnected these might have appeared. We have now reached a stage where we should frame a cogent theory about the intrinsic *nature of heat* that will enable us to understand and correlate better the observed facts, the most fundamental of which may be summed up as follows: (*i*) Heat expands bodies; (*ii*) heat is conserved, *i.e.*, whenever there is exchange of heat between bodies, the total amount of heat lost is always equal to that gained; (*iii*) the change of state from solid to liquid or liquid to gas is always accompanied by absorption of heat without rise in temperature (latent heat); (*iv*) different bodies have different capacities for heat and different thermal conductivities; (*v*) radiant heat is transmitted in space, like light in wave-motion with the velocity of light.

R. Clausius

From very early times, two rival theories concerning the nature of heat were proposed. One of them, based on the pre-historic method of making fire by rubbing together two pieces of stick, contended that heat must be some kind of *frictional motion*, which is now known as the *dynamical theory of heat*. The other, based on the fact that heat could pass easily from a hot body to a cold one, asserted that heat must be some kind of fluid, which is now known as the *caloric theory of heat*. Though neither of the two theories was really founded on any well-tested fact, the latter view was preferred and generally accepted up to the end of the 18th century. But the experiments of Rumford conducted in 1798, those of Davy in 1812 and of Joule from 1840 to

1878 progressively established the fact that *heat is a form of energy arising from mechanical motion of material particles*—thus in favour of the dynamical theory, accompanied by a slow and painful rejection of the much favoured caloric theory.

Another theory concerning the nature and behaviour of matter in general, known as the *kinetic theory*, whose foundation was laid in 1730 by Daniel Bernouilli to be subsequently placed on a firm mathematical basis by Clausius and Maxwell in the middle of the 19th century, contributed much to the final downfall of the caloric theory and the universal acceptance of the dynamical theory. It was Clausius and Krönig, who were the first, in 1857, to state in clear terms *that heat consists in the motion of molecules of matter*. Till the beginning of the present century, however, no direct experimental proof of the actual existence of the molecules or of their motion was available. Since then many evidences have been gathered in favour of the kinetic theory, so that its support to the dynamical nature of heat may now be considered to be definite and final.

The aim in this chapter is to give a brief account of these theories, to see why and how they were proposed, and then try to explain and correlate thermal and other allied phenomena in terms of the now accepted, kinetic theory of matter.

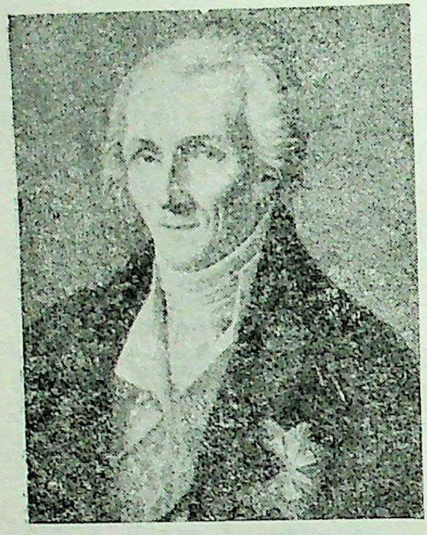
THE CALORIC THEORY OF HEAT

According to this theory, heat is considered to be a *kind of fluid*, called the *caloric*, to which different properties are attributed in order to explain the various thermal phenomena. Thus, it is supposed to be *all pervading*, *indestructible* and *uncreatable*, since it raises the temperature of any body to which it is added and lowers that of any body from which it is removed ; it must be *imponderable* since bodies do not increase in weight on mere heating ; it is *highly elastic* with its *particles repelling one another* strongly, which explains the expansion of bodies when heated as well as the emission of heat and light by bodies in combustion. The caloric always flows from a body at a higher temperature to a body at a lower temperature even as a liquid flows from a higher to a lower level. Production of heat by friction is compared to the oozing out of water from a sponge when squeezed ; the caloric when thus squeezed out manifests itself as heat. These facts show that the caloric is a *material fluid*, though imponderable and all pervading. The particles of the caloric though self-repellent, are strongly attracted and held by the molecules of matter in the interstices between them ; but different kinds of matter attract the caloric with unequal forces, which explains the different thermal capacities and conductivities of different bodies. The latent heat phenomenon is ingeniously explained as follows : Supposing that the caloric and the solid, say, form a sort of chemical compound, the liquid, which has its own properties, does not exhibit those of either constituent ; hence the heating property of the caloric is suppressed and it does not produce any rise in temperature.

This ancient theory has thus the great merit of explaining practically all the observed phenomena connected with heat, though in a rather crude and rudimentary manner. Further, when we consider the modern conceptions of the great similarity between thermal and electrical conductivities of bodies, which are attributed to the movement of material particles, the electrons, of the mass-energy equivalence of the theory of relativity and of the double aspect, corpuscular and wave of radiation, we can perhaps understand why the caloric theory has been held so firmly, almost by intuition, for such a long time and by so many eminent thinkers. Of course, the early propagandist of the theory, the so-called calorists, were not aware of these modern refinements and hence their opinion was contradicted by new discoveries about the intrinsic nature of heat.

THE DYNAMICAL THEORY OF HEAT

Serious doubts began to be cast on the caloric theory towards the end of the 18th century, as a result of some observations made by Rumford, an artillery engineer. While engaged in boring the barrel of a cannon from a solid cylindrical rod, he noticed that the chips of steel thrown off by the boring tool were very hot. In order to determine more precisely the source of this heat, he repeated his experiment, in 1798, with a blunt borer which could not scrape off much metal and found that *an inexhaustible amount of heat could be produced by mere friction*. The calorists had tried to explain away the great amount of heat contained in the chips cut off, by asserting that when a solid was reduced to a powdered state its thermal capacity decreased, so that a rise in temperature occurred without the addition of any heat. This assertion was evidently wrong, since there is no difference in the specific heat of a substance in the bulk or powdered state. Further, the caloric theory, according to which any body could contain only a limited quantity of the caloric, was quite unable to account for the finding of Rumford that as long as work was done by friction heat could be obtained without limit. Hence, Rumford rightly rejected the caloric theory and stated that *heat was only a kind of motion and whenever motion disappeared it reappeared as heat in an exact proportionality.* He even made an estimate of the ratio between the work done by friction and the amount of heat thereby produced, which was later called the *mechanical equivalent of heat* J, and obtained a value close to the one now accepted.

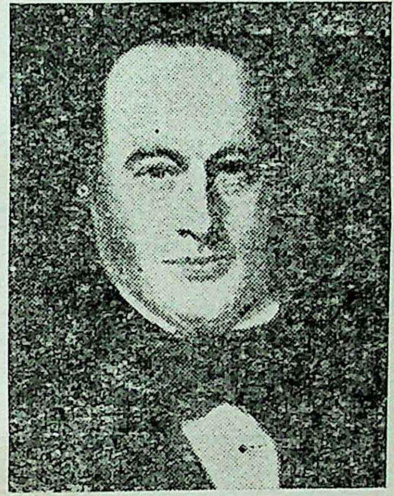


Rumford

Humphry Davy

In 1812, Humphry Davy, in order to convince further the "die-hard" calorists of their error, performed the following crucial experiment. Mounting suitably two blocks of dry ice and rubbing them together, he succeeded to melt away the two blocks very nearly and noticed that the melting was confined to the two surfaces that were rubbed against each other. Precautions were taken not to communicate any heat to the blocks of ice from outside by mounting them in a vacuum and rubbing them by means of a clock work. From the result obtained, Davy argued as follows :— It is admitted by all that water has a greater capacity for heat than ice. But, according to the caloric theory, water produced by friction of ice should have its capacity for heat lowered, which is therefore not true to facts. Hence the caloric theory is wrong. The correct explanation is that *heat is produced by the motion of material particles caused by friction.* Now we know that this is really the case, since, first of all, the specific heat of water is much greater than that of ice and, secondly, radiant heat, like light, arises from the vibration of the molecules of the source and is propagated in space in the form of wave motion.

But the works of Rumford and Davy and their valuable conclusions were soon forgotten, until, in 1840, Dr. Joule undertook a series of experiments, which were conducted during a period well over three decades, to put the matter beyond all doubt. Following the suggestion of Rumford that there existed a relation of proportionality between the mechanical work done and the amount of heat thereby produced, he concentrated his attention on the measurement of the ratio of the work spent W and the heat H developed. Making arrangements to do the work in different ways, he was able to show that a given amount of work always produced the same quantity of heat in all cases, so that W/H was a constant, later represented by the symbol J, known as *Joule's constant* or the *mechanical equivalent of heat*,



J.P. Joule

$$\frac{W}{H} = J.$$

The value of J will evidently depend on the units of work and of heat chosen. It is usually expressed in *ergs per calorie* ; it may be expressed also as foot pounds per B. Th. U. An immediate consequence of this result is that *heat is a form of energy like mechanical work*.

Joule's experiments. His first experiment consisted in producing heat by churning water contained in a calorimeter by means of brass paddles which were kept revolving by a string wound over a drum, passing over two pulleys and carrying equal weights at its ends. The amount of work done was determined by observing the height through which the weights fell. The amount of heat generated could be found by measuring the rise in temperature of the water. Thus, if M is the mass of each weight and h the height through which they fall n times, the work done is $2nMgh$ ergs. If m is the mass of water, w the water equivalent of the calorimeter and paddles and θ the rise in temperature, the heat developed is $(m + w)\theta$ calories. Hence

$$J = \frac{W}{H} = \frac{2n\,M\,g\,h}{(m + w)\theta} \text{ ergs per calorie.}$$

In the second and third sets of experiments the water was replaced by mercury and the paddles used were of iron. In the fourth and fifth sets heat was produced by the friction of two rings rubbing against each other immersed in a pool of mercury. In the sixth series of experiments work was done by forcing water through narrow tubes, while in the seventh heat was produced by compressing a given mass of gas. Finally, in the eighth series, Joule designed an electrical method of producing heat. The results he obtained by these methods in which the way of doing work or of producing heat was varied, were as follows :—

Method	*J in ergs per calorie*
Friction between brass paddles and water	$4{\cdot}161 \times 10^7$
Friction between iron paddles and mercury	$4{\cdot}169 \times 10^7$
Friction between iron rings in mercury	$4{\cdot}174 \times 10^7$
Forcing water through narrow tubes	$4{\cdot}168 \times 10^7$
Compression of air	$4{\cdot}36 \times 10^7$
Electrical method	$4{\cdot}52 \times 10^7$

It is seen that the values of the first four methods agree with one another within the limits of experimental error. The somewhat large divergence of the last two values is due to imperfections in the techniques used, although the magnitude is of the right order. These results show not only that there is a definite relation between mechanical work and heat, independent of the manner in which work is done, but also that the heat is a form of energy, like mechanical and electrical energies.

Hirn's experiments. Hirn, in 1862, made some quantitative measurements on the converse process employing a steam engine (which had already come into use) just to make quite sure that Joule's conclusion was correct. He measured the amount of steam entering the cylinder of a steam engine in a given time at a known temperature and pressure, from which the quantity of heat supplied could be estimated. The heat rejected by the engine was found by receiving the waste steam into a calorimeter during the same time. He also estimated the quantity of heat lost in cooling and other causes. The net amount of heat which was converted into work could then be obtained. He measured the amount of work done by the engine in the same time and thus was able to find the number of ergs of work done by the engine when one calorie of heat disappeared. He got a value of $4{\cdot}18 \times 10^7$ ergs per calorie in close agreement with Joule's values, which proved conclusively that when mechanical work is done, all of it is converted into heat.

Mayer's work. While Joule was performing his classical experiments, Mayer devised an ingenious means of calculating J from the values of the two specific heats of a gas. We have already seen that these two quantities are related to each other by the expression

$$C_p - C_v = \frac{R}{J} \qquad (Cf.\ \text{p. } 141)$$

Taking hydrogen, $C_p = 3{\cdot}41$ calories per gram per °C and $C_v = 2{\cdot}41$ calories per gram per °C.

R, the gas constant, can be found as follows : 1 gram-molecule of hydrogen (*i.e.*, 2 gms.) occupies a volume of 22·4 litres at N.T.P. Hence 1 gm. of hydrogen at 76 cm. pressure and 0°C or 273°K occupies a volume of 11,200 c.cs. Using the relation

$$pv = RT \quad \text{or} \quad R = \frac{pv}{T}$$

$$R = \frac{(76 \times 980 \times 13{\cdot}6) \times 11200}{273}$$

$$= 4{\cdot}14 \times 10^7 \text{ ergs per gm. per °C.}$$

$$\text{Hence } (3{\cdot}41 - 2{\cdot}41) \text{ calories} = \frac{4{\cdot}14 \times 10^7}{J} \text{ ergs}$$

$$\text{or} \qquad J = 4{\cdot}14 \times 10^7 \text{ ergs per calorie.}$$

The agreement between this value and those of Joule and Hirn is fairly satisfactory, given the fact that the equation used by Mayer is true only for an ideal gas.

Rowland's experiments. In 1879, Rowland undertook the accurate determination of the mechanical equivalent of heat J.

Following the opinion of Joule that the method of producing heat by the friction of paddles rotating in a liquid was capable of giving the most accurate results, he employed that same method but with further improvements, in order to obtain results to an accuracy of 1 in 2,000. The two chief drawbacks of Joule's experiment were : (*i*) The rate of rise of temperature was very small (about 0·6°C per hour) so that the radiation loss was large and hence could not be corrected for accurately. Rowland overcame this difficulty to a great extent by a special device of rotating the paddles continuously and rapidly inside the calorimeter suspended by a torsion wire and maintained steady by a suitably applied couple, in order that a greater amount of work could be done in a shorter time with the consequent higher rate of rise in temperature (about 40°C per hour). (*ii*) The mercury thermometers used by Joule were not standardised, which, therefore, introduced errors of the order of 1 to 2%. Rowland took care to correct his mercury thermometers to a standard gas scale of temperature.

The apparatus used is shown diagrammatically in Fig. 143. The calorimeter C fitted with a set of vanes V is firmly attached to a vertical shaft S to which is fixed a circular disc D, the whole being suspended by a torsion wire W. A set of paddles P is made to rotate inside the calorimeter by a small steam engine (not shown in figure) attached by a belt to a pulley R on the axle of the paddles passing out of the calorimeter from below. The number of rotations made by the paddles is automatically recorded on a suitably geared mechanical counter. The paddles and the vanes have a large number of holes in them in order to prevent rotation of water in the calorimeter along with the paddles. The rapid revolution of the paddles tend to rotate the calorimeter in the same direction on account of fluid friction. This is prevented by the torsion wire and couple applied by the use of suitable equal weights MM acting on the disc D through strings passing over the pulleys PP, on opposite sides and wound round D. A horizontal arm A is attached to the vertical shaft S and

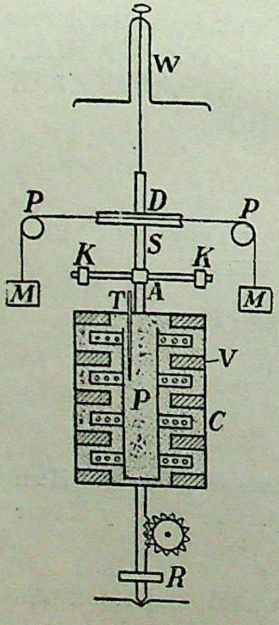


Fig. 143. Rowland's apparatus.

carries sliding weights KK whose positions on the arm can be adjusted so as to vary the moment of inertia of the suspended part. The calorimeter contains a known mass of water, whose temperature is measured by a sensitive mercury thermometer T inserted into the perforated central shaft of the paddles.

In performing the experiment, the initial temperature θ_1 of the water in the calorimeter is noted and the paddles are set rotating. The weights MM are quickly adjusted so as to keep the calorimeter steady in its equilibrium position. The rotation is continued until a decent rise in temperature is obtained, the number of revolutions being recorded by the counter and the temperature being read at frequent intervals. In this manner a set of readings for the number of revolutions and the corresponding rise in temperature is obtained, from any pair of which J can be calculated :—

If the paddles make n revolutions against the couple due to the two weights M grams, acting on the disc D of diameter d cms. the work done against the couple is given by $W = 2\pi n \, Mgd$ ergs.

If m is the weight of water taken in the calorimeter, w the water equivalent of the calorimeter, paddles, vanes, etc., and $(\theta_2 - \theta_1)$ the corresponding rise in temperature of the calorimeter and contents, the heat produced is given by $H = (m + w)\,(\theta_2 - \theta_1)$ cals.

Hence $$J = \frac{W}{H} = \frac{2\pi n \, Mgd}{(m + w)\,(\theta_2 - \theta_1)} \text{ ergs/cal.}$$

The cooling correction is estimated by allowing the calorimeter to cool with the paddle turning slowly to stir the water. The heat produced by this stirring is calculated and allowed for.

Corrections are also applied for the torsional couple, for the weights in air which must be reduced to vacuum, etc.

The readings of the mercury thermometer is reduced to the standard constant volume hydrogen scale.

The results obtained by Rowland for J at various temperatures are given below :

Temperature (°C)	*J in ergs per calorie*
10	$4{\cdot}196 \times 10^7$
15	$4{\cdot}188 \times 10^7$
20	$4{\cdot}181 \times 10^7$
25	$4{\cdot}176 \times 10^7$
30	$4{\cdot}174 \times 10^7$
35	$4{\cdot}175 \times 10^7$

It is seen that *the value of J varies regularly with temperature.* This implies that the specific heat of water is not constant but varies with temperature, which is of significance, as it makes it necessary to specify the precise range of temperature in the definition of the unit of heat, the calorie, as already indicated (*Cf.* p. 138). Overlooking this slight variation, the average value of J is 4·18 × 10^7 ergs per calorie, which is considered to be fairly accurate.

The result thus obtained by Joule, Hirn, Mayer, Rowland and others, which established beyond doubt that heat and work are mutually convertible, with a definite relation between the two, has been generalised into the famous *first law of thermodynamics*, as we shall see in the last chapter. For the present, it is enough to note that the dynamical theory, conceiving heat as a form of energy arising from a kind of motion, finally triumphed over the rival caloric theory, thanks to the corroborative researches described above. We shall conclude this subject by briefly describing the different methods used later for determining J.

Methods used for determining J are :—

(*i*) Searle's friction-cones apparatus.

(*ii*) Callendar's friction machine.

(*iii*) Joule's method.

(*iv*) Callendar and Barnes continuous flow method.

These methods are based on the same principles as utilised by Joule in his researches, chiefly those, in which heat is generated either by mechanical friction or by supply of electrical energy, and which are considered capable of yielding accurate results. The apparatus employed are, however, much more refined than the simple designs of the original experiments. The last two are *electrical methods*, which have already been described in detail in connection with the measurement of the specific heat of liquids (*Cf.* pp. 133-6). It is readily seen there that if the specific heat of the liquid is known, the mechanical equivalent of heat J is obtained in these methods. Hence we shall describe here only the first two.

Searle's friction-cones apparatus offers a *simple laboratory method* of finding the value of J. The apparatus, first devised by Searle, is shown in Fig. 144. It consists of two brass conical cups B and C fitting smoothly one into the other. The outer cup B is fitted inside a cylinder A with non-conducting ebonite pieces. The cylinder A is mounted on a vertical spindle E, which can be driven by a belt connecting the grooved pulley G fixed to E to a small motor or a driving hand-wheel. As the cylinder rotates, the outer conical cup B will also rotate, the number of revolutions being registered by a counter N geared to the spindle. The inner cup C serves as a calorimeter and contains water, a sensitive thermometer T suspended from a stand and a stirrer S. A circular wooden disc DD having a grooved edge is fixed on the top of C with the help of two pins of the upper rim of C. To ensure good contact and sufficient friction between the two cups, a ring-shaped weight WW is placed on D. A string attached to a point on the rim of D, goes round its grooved circumference, passes over a pulley P and is kept in tension by suitable weights placed in a pan M attached at the free end. It is this force on the string which prevents the inner cup from rotating while the outer is made to spin about its axis.

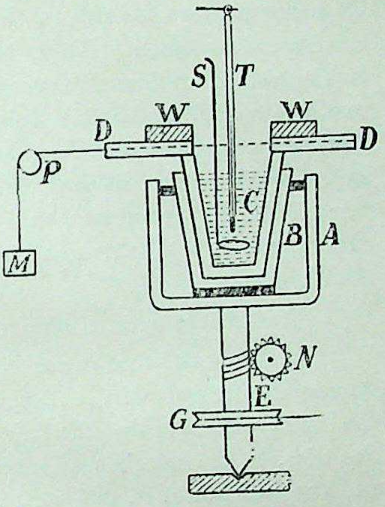


Fig 144. Searle's apparatus for J.

To perform the experiment the two cups are cleaned and weighed and their water equivalent determined, assuming the specific heat of the material. Care is taken to see that there is a suitable uniform friction between the cups. To obtain this, the surfaces in contact should be clean and free from grit ; a trace of oil on the surfaces will be often found useful in producing the desired effect. A known mass of water is taken in the inner cup to occupy about 4/5 of its capacity and the initial temperature of the water and the reading of the counter are noted. A suitable weight is put in the pan and the speed of rotation of the outer cup is adjusted by trials so that the pan with its load remains steady. The driving wheel must be turned as uniformly as possible, jerks being avoided. The hand-wheel is rotated until the temperature rises to about 5°C. The water is well stirred and its final temperature is noted. Correction for radiation may be applied using any one of the simpler methods mentioned in calorimetric experiments, since the rise in temperature is not very great. Moreover, the aim should be to produce an appreciable rise of temperature in a very short interval of time, which can be done by using a large weight in the pan and rotating the spindle at a corresponding speed. If the time interval is small, the total heat lost by radiation becomes very small and negligible. The counter reading is again taken at finish. The difference between its two readings gives the total number of revolutions made by the outer cup. It is to be noted that when once the work of rotation has been started the experiment should not be interrupted, otherwise the experiment has to be done all over again. The radius of the disc D is measured.

From these data, the value of J is calculated as follows :—

In the position of equilibrium of the pan, which is maintained during the experiment, the turning moment due to the tension on the string just balances the frictional couple. If r is the radius of the disc, n the number of revolutions made, M the mass of the pan and the weights in it, the work done against friction is given by

$$W = Mg \times 2\pi r \times n \text{ ergs.}$$

If m is the mass of water taken, θ_1 and θ_2 its initial and final temperatures and w the water equivalent of the two cups, the heat produced due to friction is given by $H = (m + w)(\theta_2 - \theta_1)$ calories.

$$\therefore \qquad J = \frac{W}{H} = \frac{2\pi r n Mg}{(m + w)(\theta_2 - \theta_1)} \text{ ergs/cal.}$$

Callendar's apparatus, shown in Fig. 145, consists of a cylindrical calorimeter C mounted on a horizontal shaft S rotated by a motor or a hand-wheel H. The heat is produced by the friction of a silk belt A pressing against the outer surface of the calorimeter. A sensitive thermometer T measures the temperature of the water in the calorimeter. The work done due to friction is determined by using the silk belt as a brake tester as follows :—Two ribbons of silk whose ends are connected by two ebonite cross-bars are wound once round the calorimeter. A third ribbon attached to the middle of one of the cross-bars is wound in the opposite direction and

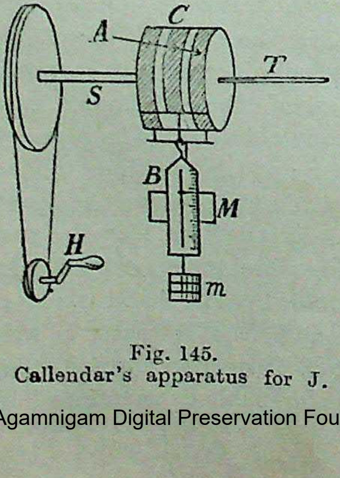


Fig. 145.
Callendar's apparatus for J.

lies symmetrically between the outer two. A heavey load M (about 5 K gms.) is attached to the end of the first two ribbons, while a spring balance B and a small load m (about 300 gms.) are attached to the end of the central ribbon. When the calorimeter is being rotated at the proper speed, the heavier load is kept steady, the spring balance automatically controlling the tension along the ribbons. If m' is the reading of the spring balance under these conditions, the force against which work is done is readily seen to be $(M - m + m')\,g$. If the calorimeter has been rotated n times and if its diameter is d, the work done $= \pi\, n\, d\, (M - m + m')\, g$. The heat produced is measured by the rise in temperature of a known mass of water contained in the calorimeter. If w be the amount of water taken, w' the water equivalent or the calorimeter, θ_1 and θ_2 the initial and final temperatures of the water, the heat generated by friction $= (w + w')\,(\theta_2 - \theta_1)$

$$\therefore \qquad J = \frac{\pi\, n\, d\, (M - m + m')g}{(w + w')\,(\theta_2 - \theta_1)}$$

THE KINETIC THEORY OF HEAT

Experiments described above clearly established that heat is a form of energy intimately connected with motion in matter. The next question, which naturally suggests itself, is : *What sort of energy and what kind of motion ?* The answer to this question is given by the *kinetic theory* of matter.

According to this theory, every substance, whether a solid, liquid or gas, consists of a very large number of discrete particles called molecules. A molecule is the smallest particle of a substance which can exist in a free state and possesses all the characteristic properties of the substance. The molecules of a substance are in a state of incessant motion, whose velocity increases with temperature. In *solids* the molecules are very closely packed and attract each other with a large force of cohesion. They cannot move about freely but can only vibrate about a mean position, which accounts for the definite shape and volume of solids. The molecules in a *liquid* are farther apart than in a solid and attract each other with smaller force of cohesion. They cannot easily leave the liquid but are free to move about anywhere within the liquid, which explains why a liquid has a definite volume but no shape of its own. In a *gas* the molecules are very much farther apart than those of a solid or liquid. The force of attraction between the molecules of a gas is almost negligible and the molecules are free to move about over the entire space available. This is why a gas has neither a shape nor volume of its own. On this fundamental conception of the kinetic theory, *viz.*, the existence of molecules in incessant motion, we have already explained several of the thermal properties of the three states of matter, such as expansion, change of state, melting and boiling points, cooling due to evaporation, etc.

The study of the kinetic theory was first approached by applying it to matter in the gaseous state which is governed by simple and definite laws. Thus, Bernouilli, in 1730, was able to explain, for the first time, Boyle's law by molecular motions, and for this reason he is considered as the *father of the kinetic theory*. From the middle of the 19th century, the kinetic theory of gases was greatly developed by Clausius, Maxwell, Boltzmann, Jeans, Van der Waals, Lorentz and Rayleigh, covering almost the entire field of the different phenomena related with gases. Attempts have been made, in recent years, to extend the theory to liquid and solid states with some success; but the kinetic theory of liquids and solids is much more complicated and still remains in a comparatively undeveloped state and hence will not be treated in this book. We shall be, therefore, concerned only with the kinetic theory of gases.

Fundamental assumptions. The kinetic theory of gases is based on the following main assumptions, first stated by Clausius :—

(*i*) The molecules of a gas are considered to be rigid, perfectly elastic, solid spheres, identical in all respects such as mass, form, etc. They are, however, of negligible size as compared with their distance apart.

(*ii*) The molecules are in a state of incessant random motion, moving in all directions with all possible velocities. The gas is said to be in a state of molecular chaos.

(*iii*) The molecules in their motion collide with one another and with the walls of the containing vessel. At each collision their velocities are altered in direction and magnitude; yet in the steady state the collisions do not affect the molecular density of the gas, *i.e.*, the number of molecules per unit volume of the gas remains constant.

(*iv*) The collisions are perfectly elastic and there are no forces of attraction or repulsion between the molecules, which means that the energy of the gas is all kinetic.

(*v*) The time spent in a collision is negligible as compared with that during which the molecules are moving independently.

(*vi*) Between collisions the molecules move in a straight line with uniform velocity. The distance between two collisions is called the *free path* of the molecule ; the average distance travelled by a molecule between successive collisions is known as the *mean free path.*

These assumptions are justifiable, since we are constructing a general theory which should represent the behaviour common to all gases and hence should not include any factors which may vary from one gas to another.

With these postulates the bulk properties of a gas can be explained by the application of the laws of probability to a system in dynamic equilibrium, *i.e.*, on the basis of the most probable behaviour of the largest number of molecules in a given volume. Let us now see how this is done.

1. Pressure of a gas. The molecules in their random motion will not only collide with one another, but also impinge on the walls of the containing vessel, thereby transmitting a definite momentum to the walls. Since the number of molecules making such impacts with the walls is very great, the walls will experience an almost continuous force, which referred to unit area is pressure. Hence, according to the kinetic theory, the pressure exerted by a gas is merely the total momentum communicated to the walls of the containing vessel per second per unit area due to the impacts of the molecules of the gas. An expression for the pressure exerted by a gas may, therefore, be obtained as follows :—

Let the gas be contained in a cubical vessel of side l with perfectly elastic walls and let n represent the very large number of molecules in the vessel (Fig. 146). Considering any one of these molecules having a velocity c_1 in a certain direction, this velocity can be resolved into three components u_1, v_1 and w_1 parallel to three co-ordinate axes, X, Y and Z, which are assumed parallel to the sides of the cube. Then

$$c_1^2 = u_1^2 + v_1^2 + w_1^2 \qquad \dots (1)$$

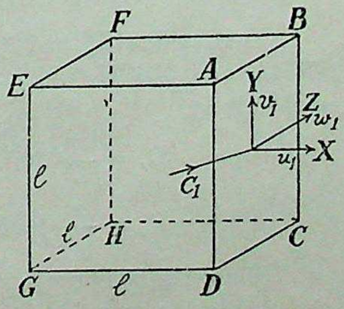


Fig. 146.

If the molecule considered strikes the face ABCD of the cube, it will communicate a momentum to the face equal to mu_1 where m is the mass of the molecule, since the component velocity which is effective is the one normal to the face. Further, since the collision is perfectly elastic, the molecule will rebound from the face with the same velocity u_1, so that the change in its momentum produced by the impact is

$$mu_1 - (-mu_1) = 2mu_1$$

After recoil, the molecule travels to the opposite face EFHG, collides with it, rebounds and travels back to the face ABCD, after covering a distance $2l$. The time between the successive collisions on ABCD is, therefore, equal to $2l/u_1$. From this we get the number of collisions per second, which the molecule makes with ABCD as $u_1/2l$. Hence the rate of change of momentum

$$= 2mu_1 \times u_1/2l = mu_1^2/l$$

Now, according to Newton's second law, the rate of change of momentum = impressed force. If f_1 is the impressed force,

$$f_1 = mu_1^2/l$$

Similarly the force f_2 due to the impact of another molecule having a velocity c_2, whose three rectangular components are u_2, v_2 and w_2, is given by

$$f_2 = mu_2^2/l$$

Hence, the total force F_x on the face ABCD due to impacts of all the n molecules is given by

$$F_x = \frac{m}{l}(u_1^2 + u_2^2 + \ldots\ldots + u_n^2) \quad \ldots (2)$$

Since pressure is force per unit area, the pressure P_x on ABCD is given by

$$P_x = \frac{F_x}{l^2} = \frac{m}{l^3}(u_1^2 + u_2^2 + \ldots\ldots + u_n^2) \quad \ldots (3)$$

Similarly, if P_y and P_z represent the pressures on the faces EFBA and FBCH which are perpendicular to the Y- and Z-axes respectively,

$$P_y = \frac{m}{l^3}(v_1^2 + v_2^2 + \ldots\ldots + v_n^2) \quad \ldots (4)$$

$$P_z = \frac{m}{l^3}(w_1^2 + w_2^2 + \ldots\ldots + w_n^2) \quad \ldots (5)$$

Since the pressure exerted by a gas is the same in all directions, the average pressure P of the gas is given by

$$P = \frac{P_x + P_y + P_z}{3}$$

$$= \frac{m}{3l^3}\{(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) + \ldots\ldots + (u_n^2 + v_n^2 + w_n^2)\} \qquad \ldots (6)$$

Since $l^3 = \mathrm{V} =$ volume of the cube, and

$c_1^2 = u_1^2 + v_1^2 + w_1^2$, $c_2^2 = u_2^2 + v_2^2 + w_2^2$ and so on

$$\mathrm{P} = \tfrac{1}{3}\frac{m}{\mathrm{V}}(c_1^2 + c_2^2 + \ldots\ldots + c_n^2)$$

$$= \tfrac{1}{3}\frac{mn}{\mathrm{V}}\mathrm{C}^2 \qquad \ldots (7)$$

where $\mathrm{C}^2 = \dfrac{c_1^2 + c_2^2 + \ldots + c_n^2}{n}$, known as the *mean square velocity* of the molecules.

If M be the total mass of the gas, $\mathrm{M} = mn$, and

$$\mathrm{P} = \tfrac{1}{3}\frac{\mathrm{M}}{\mathrm{V}}\mathrm{C}^2 \qquad \ldots (8)$$

Root mean square (*R.M.S.*) *velocity.* C is called the root mean square velocity of the molecules and is equal to the *square root of the mean of the squares of the velocities of the individual molecules* which is evidently not the same as the mean of the velocities of the different molecules. It can be estimated as follows :—

Since $\dfrac{\mathrm{M}}{\mathrm{V}} = \rho$, the density of the gas,

$$\mathrm{P} = \tfrac{1}{3}\rho\,\mathrm{C}^2 \qquad \ldots (9)$$

$$\therefore \quad \mathrm{C} = \sqrt{\frac{3\mathrm{P}}{\rho}}$$

Examples. (*i*) In the case of *air* at N.T.P.,

$\mathrm{P} = 76 \times 13{\cdot}6 \times 981$ dynes per sq. cm.

$\rho = 0{\cdot}00129$ gm./c.c. at N.T.P.

$$\therefore \quad \mathrm{C} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{0\,00129}}$$

$$= 4{\cdot}856 \times 10^4 \text{ cms./sec.}$$

(*ii*) For *hydrogen* at N.T.P.,

$\rho = 0{\cdot}000089$ gm./c.c.

$$\therefore \quad \mathrm{C} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{0{\cdot}000089}}$$

$$= 18{\cdot}4 \times 10^4 \text{ cms./sec.}$$

(*iii*) For *oxygen* at N.T.P.,

$\rho = 16 \times {\cdot}000089$, assuming that the density of oxygen is 16 times that of hydrogen.

$$\therefore \qquad C = \frac{18{\cdot}4 \times 10^4}{4} = 4{\cdot}6 \times 10^4 \text{ cms./sec.}$$

Relation between pressure and kinetic energy. Equation (9) can be put as

$$P = \tfrac{2}{3} \cdot \tfrac{1}{2} \rho C^2$$

Here $\frac{1}{2} \rho C^2$ represents the mean kinetic energy per unit volume of the gas (E), so that

$$P = \tfrac{2}{3} E \qquad \dots (10)$$

Thus, the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy of translation per unit volume.

2. Interpretation of temperature. According to relation (7) the pressure exerted by a gas made up of n molecules and occupying a volume V is given by

$$P = \tfrac{1}{3} \frac{mn}{V} C^2$$

or

$$PV = \tfrac{1}{3}\, m\, n\, C^2$$

If V is the volume occupied by a gram-molecule of the gas and M the molecular weight of the gas, since then $M = mn$,

$$PV = \tfrac{1}{3} MC^2 \qquad \dots (1)$$

Now, making use of experimental law, known as the perfect gas equation *viz.*,

$$PV = RT \quad (\textit{Cf.}\ \text{p. } 21), \qquad \dots (2)$$

from (1) and (2), we get

$$\tfrac{1}{3} MC^2 = RT$$

or

$$C^2 = \frac{3R}{M} \cdot T \qquad \dots (3)$$

This shows that the mean square velocity (C^2) is directly proportional to the absolute temperature T. At $T = 0$, $C^2 = 0$, or $C = 0$. Hence *the absolute zero of temperature is that temperature at which the molecular translational velocities of a gas are reduced to zero.*

From (3), we get

$$\tfrac{1}{2} MC^2 = \tfrac{3}{2} RT \qquad \dots (4)$$

Dividing both sides by N, the number of molecules in 1 gram-molecule of the gas, called the *Avogadro's number*,

$$\tfrac{1}{2} \frac{M}{N} C^2 = \tfrac{3}{2} \frac{R}{N} T$$

But $\frac{M}{N} = m$ and $\frac{R}{N} = k$, a constant, known as the *Boltzmann's constant.*

$$\therefore \qquad \tfrac{1}{2}mC^2 = \tfrac{3}{2}\,kT \qquad \ldots (5)$$

Thus the *mean kinetic energy per molecule in a given mass of gas is proportional to the absolute temperature of the gas.* That is, to every uniform temperature there is a corresponding uniform distribution of kinetic energy and the molecular collisions furnish the mechanism which leads to the equalisation of temperature.

Examples. (*i*) At what temperature will the root mean square velocity of hydrogen be double of its value at N.T.P., pressure remaining constant.

From relation (4), $C \propto \sqrt{T}$

Let the velocity at N.T.P., *i.e.*, at T_0°K be C_0.

If T°K is the temperature required, the velocity C at that temperature $= 2C_0$

$$\therefore \qquad \frac{C}{C_0} = \frac{2C_0}{C_0} = \sqrt{\frac{T}{T_0}}$$

$$\text{or} \qquad 4 = \frac{T}{T_0}$$

$$\therefore \qquad T = 4T_0 = 4 \times 273 = 1092°\text{K}$$

$$= 1092 - 273 = 819°\text{C}$$

Note. The R.M.S. velocity at any temperature θ°C is given by

$$C = C_0\sqrt{\frac{273 + \theta}{273}}$$

$$= \sqrt{\frac{3P\,(273 + \theta)}{\rho\,.\,273}}, \text{ since } C_0 = \sqrt{\frac{3P}{\rho}}$$

$\therefore$ R.M.S. velocity of air (ρ at N.T.P. $= \cdot 001296$)

$$\text{at } -100°\text{C} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 980\,(273 - 100)}{\cdot 001296 \times 273}}$$

$$= 1{\cdot}48 \times 10^4 \text{ cms./sec.}$$

$$\text{at } 1000°\text{C} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 980\,(273 + 1000)}{\cdot 001296 \times 273}}$$

$$= 10{\cdot}87 \times 10^4 \text{ cm./sec.}$$

(*ii*) Find the molecular kinetic energy of 1 gram of helium at N.T.P. What will be the energy at 100°C ?

From relation (4), $\frac{1}{2}C^2 = \frac{3}{2} \cdot \frac{R}{M} \cdot T$

Since $R = 8{\cdot}3 \times 10^7$, $T = 273°K$ and $M = 4$, the kinetic energy of 1 gm. of helium at N.T.P.

$$= \frac{1}{2} \times 1 \times C^2 = \frac{3}{2} \cdot \frac{8{\cdot}3 \times 10^7 \times 273}{4} = 8{\cdot}5 \times 10^9 \text{ ergs.}$$

$$\text{Energy at } 100°C = \frac{8{\cdot}5 \times 10^9 \times 373}{273} = 1{\cdot}16 \times 10^{10} \text{ ergs.}$$

(*iii*) The kinetic energy of a molecule of hydrogen at 0°C is $5{\cdot}64 \times 10^{-14}$ ergs and the molecular constant (R) $= 8{\cdot}32 \times 10^7$ ergs. Calculate Avogadro's number (N).

The kinetic energy of a molecule $= \frac{1}{2}m\,C^2 = 5{\cdot}64 \times 10^{-14}$ ergs.

From relation (3), $\frac{1}{3}Nm\,C^2 = RT$

$$\therefore N = \frac{3RT}{mC^3} = \frac{3 \times 8{\cdot}32 \times 10^7 \times 273}{2 \times 5{\cdot}64 \times 10^{-14}} = 6{\cdot}08 \times 10^{23}.$$

3. Gas laws—(*a*) *Boyle's law.* According to the kinetic theory of gases, the pressure p of a gas is given by

$$p = \frac{1}{3} \frac{mn}{v} C^2$$

Hence $pv = \frac{1}{3} mnC^2 = \frac{1}{3} MC^2$, where M is the mass of the gas. When the temperature is kept constant, the mean square velocity is constant. Hence for a given mass of gas (*i.e.*, M constant) and at a given temperature, pv = constant, which is Boyle's law.

(*b*) *Charles' law.* Since $pv = \frac{1}{3} MC^2$ and MC^2 varies as T, pv also should vary as T. This is Charles' law which may be stated in two ways: The volume of a gas at constant pressure is directly proportional to the absolute temperature or the pressure of a gas at constant volume is directly proportional to the absolute temperature.

(*c*) *Avogadro's law.* This law states that at the same temperature and pressure equal volumes of all gases contain the same number of molecules. To deduce this from the kinetic theory, let us consider unit volume (1 c.c.) of two different gases which are at the same temperature T and the same pressure p. Let n_1 and n_2 be the numbers of molecules per c.c., m_1 and m_2 their masses and C_1 and C_2 their root mean square velocities in the two gases respectively.

Since the two gases exert the *same pressure*,

$$p = \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2 \qquad \dots(1)$$

Since the *temperatures are the same,* there will be no change in temperature when the two gases are mixed up. This is possible only if the mean kinetic energy per molecule in the two gases is the same. Hence

$$\tfrac{1}{2}\, m_1\, C_1^2 = \tfrac{1}{2}\, m_2 C_2^2 \qquad \ldots(2)$$

From (1) and (2), we get

$$n_1 = n_2$$

i.e., the numbers of molecules per c.c. in the two gases are equal. Extending this to any equal volumes and to any number of gases, we arrive at *Avogadro's hypothesis.*

(*d*) *Dalton's law of partial pressures.* If a number of gases having densities ρ_1, ρ_2, ρ_3...and root mean square velocities C_1, C_2, C_3... are mixed up in the same volume, the resultant pressure p, considering each set of molecules is given by

$$\begin{aligned} p &= \tfrac{1}{3}\,\rho_1 C_1^2 + \tfrac{1}{3}\,\rho_2 C_2^2 + \tfrac{1}{3}\,\rho_3 C_3^2 + \cdots \\ &= p_1 + p_2 + p_3 + \cdots \end{aligned}$$

where p_1, p_2, p_3 are the pressures which each gas would exert if it alone occupied the whole volume, which is Dalton's law of partial pressures.

(*e*) *Graham's law of diffusion* states that the rate of diffusion of a gas is inversely proportional to the square root of its density. Considering a gas of density ρ_1 diffusing into another gas of density ρ_2, in the steady state of diffusion, the pressures are the same. Hence, if C_1^2 and C_2^2 be the mean square velocities of the molecules of the two gases respectively,

$$p = \tfrac{1}{3}\rho_1 C_1^2 = \tfrac{1}{3}\,\rho_2 C_2^2$$

$$\therefore \qquad \frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

In general, $\qquad C \propto \dfrac{1}{\sqrt{\rho}}$

Thus we have succeeded to frame a theory based on the translatory motion of the molecules of a gas, which explains the nature of pressure and temperature of a gas as well as accounts for the several experimentally observed gas laws. The interpretations given apply rigorously to the ideal gas, as is to be expected from the assumptions made.

Before proceeding further with the application of the theory proposed to other thermal phenomena, it is necessary to acquaint ourselves with some more special features of the theory, such as the mean free path, Maxwell's laws of distribution of velocities and of equipartition of energy among the molecules, the atomicity of gases and the application of the degrees of freedom to the law of equipartition of energy.

Mean free path. According to the kinetic theory, the molecules of a gas are moving with very large velocities, of the order of hundreds of metres per second even at ordinary temperature. There is no force to restrain their motion. This would mean that a gaseous mass would be dissipated in no time, contrary to actual observations. Hence a serious objection was raised against the assumption of such large rectilinear velocities of the molecules. Clausius solved the difficulty by ascribing to the molecules a finite though very small size and by introducing the idea of collisions between the molecules. These two factors, molecules having finite dimensions and collisions between molecules are interdependent, since the molecules could never collide with each other if they were point-masses without dimensions. As a molecule with finite size moves forward, it is sure to collide with another molecule after a short interval and its velocity and direction of motion will be changed, so that its path will consist of a series of short ziz-zag lines limited to the confines of the vessel that contains the gas. The same process holds good for all the molecules of the gas. That the molecules of all actual gases have finite dimensions has also to be admitted in order to account for the deviations of gases from the perfect gas laws, as we shall see in the next chapter.

Granting, therefore, collisions between finite-sized molecules of a gas, the path travelled by a molecule between two consecutive collisions will be a straight line with a uniform velocity, since the molecules exert no force over one another except during collision ; hence it is called the *free path*. As these paths of a molecule between collisions will not be of the same length, the *mean free path* is a more useful quantity to be considered. It is defined as the average distance travelled by a molecule between two successive collisions. If the total path travelled in N collisions is S, then the mean free path λ is given by

$$\lambda = \frac{S}{N} .$$

We shall now derive *an expression for the mean free path* in terms of quantities which can be determined, so that the characteristics of the mean free path may be analysed.

Let us consider a gas which contains n molecules per c.c. Let σ be the diameter of each of the molecules. We make a simplifying assumption that only the molecule under consideration is in motion, while all the others are at rest. Although this assumption does not represent the actual state of affairs yet it can be legitimately used for the purpose of calculation, as is done in the determination of relative velocity between two moving bodies, where one is supposed to be at rest and the other to move with a velocity which is either the sum or difference of the velocities of the bodies according as they move in opposite or same direction.

The moving molecule will collide with all those molecules whose centres lie within a distance σ from its centre (Fig. 147). If v is the velocity of the molecule, in one second it will collide with all the molecules the centres of which lie in a cylinder of radius σ, length v, and hence in a volume $\pi \sigma^2 v$. Since the number of molecules in this cylindrical volume is $\pi \sigma^2 v n$, the number of collisions N made by the moving molecule is also $\pi \sigma^2 v n$. As the distance S traversed by the molecule in one second is its velocity v, the mean free path λ is given by

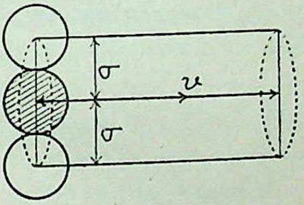


Fig. 147.

$$\lambda = \frac{S}{N} = \frac{v}{\pi \sigma^2 v n} = \frac{1}{\pi \sigma^2 n} \qquad \dots (1)$$

This equation connecting the mean free path with the molecular diameter and the number of molecules per unit volume was deduced by Clausius.

Bȯltzmann, on a more realistic assumption that all the molecules have the same average speed, derived a slightly different expression :

$$\lambda = \frac{3}{4 \pi \sigma^2 n} \qquad \dots (2)$$

Maxwell, basing himself on his more exact law of distribution of velocities, obtained a more correct expression :

$$\lambda = \frac{1}{\sqrt{2}\, \pi \sigma^2 n} \qquad \dots (3)$$

It may be noted that in all the three expressions (1), (2), (3), only the numerical constant changes, its value decreasing as the assumptions made become fewer.

In any case, *the mean free path is inversely proportional to the square of the molecular diameter*. Hence the smaller the size of the molecules, the larger will be the mean free path.

If m be the mass of a molecule, $mn = \rho$, the density of the gas

$$\lambda = \frac{m}{\pi \sigma^2 \rho}$$

Hence λ *is inversely proportional to the density of the gas*. Since the latter varies directly as the pressure and inversely as the absolute temperature, *the mean free path is inversely proportional to the pressure of the gas and directly proportional to the absolute temperature of the gas*.

Determination of the mean free path. The viscosity of gases, which can be accurately determined experimentally, offers a reliable means of estimating the mean free path, as an expression for the *viscosity of a gas* in terms of the mean free path of its molecules can be deduced on the basis of the kinetic theory as follows :—Let us suppose that a gas flows over a fixed horizontal surface OX. The velocity of the gas in contact with OX is zero and increases in the Y-direction perpendicular to the X-direction at a uniform rate, *i.e.*, with a continuous velocity gradient in the steady state of motion of the gas.

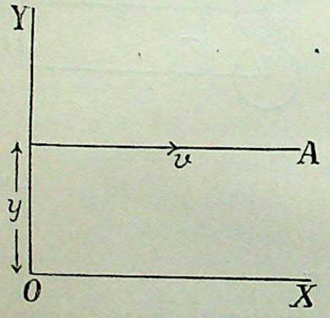


Fig. 148.

Considering a layer of gas A at a distance y from OX, let the velocity with which the gas flows in that layer be v and the velocity gradient $\frac{dv}{dy}$. (Fig. 148).

If molecules impinge on the layer A, they will rebound with the velocity of the gas at the layer, *i.e.*, v and will acquire momenta $=$ mv each. As the velocity of flow of a gas, even if it corresponds to a very violent motion, will still be very small compared with the average velocity of the individual molecules, the direction of motion of the molecules will not be changed. For the same reason, the number of molecules per unit volume will not be affected by the impact and the consequent acquired momenta. Hence we may regard, without serious error, the space between OX and the layer A to be composed of a very great number of molecular layers, the molecules of one layer differing from those of another only in the possession of different quantities of momenta, the direction of these being the same for all layers, *viz.*, the direction of flow of the gas.

It is experimentally found that the gas sets up a force opposing this *relative motion of adjacent layers.* The property by virtue of which it does this is called its *viscosity* and is estimated by a quantity known as the *coefficient of viscosity* η, which is defined as the tangential force per unit area per unit velocity gradient and is given by the relation :

$$T = \eta \frac{dv}{dy} \qquad \dots (1)$$

Hence, considering the molecules as carriers of momenta, if we can calculate the net transfer of momentum through the layer A per unit area per second, we can readily obtain an expression for the coefficient of viscosity.

Since the molecules are moving, due to thermal agitation, in all possible directions, we can imagine them to be divided into 3 parts moving in either direction parallel to the three coordinate axes, so that, on an average, 1/6th of the molecules move parallel to any one axis in one particular direction. Now, if n is the number of molecules per c.c. and $\bar{c}$ their average velocity, the number of molecules crossing the layer A upwards or downwards per unit area in one second $= n\ \bar{c}\ /\ 6.$ ... (2)

The molecules which cross from below will have a lower drift velocity than those from above. Further, since of the molecules which move towards the layer A, only those which on the average are not farther away than the mean free path λ will cross it, we may assume that the mean velocity of the molecules crossing from below is $\left(v - \frac{dv}{dy} \lambda \right)$ and of those from above $\left(v + \frac{dv}{dy} \lambda \right)$ ... (3)

Therefore total momentum carried by all the molecules moving *upwards* and crossing the layer A, per unit area per second

$$= \frac{m\ n\ \bar{c}}{6} \left(v - \frac{dv}{dy} \lambda \right)$$

Total momentum carried by all the molecules moving *downwards* and crossing the layer A, per unit area per second

$$= \frac{m\ n\ \bar{c}}{6} \left(v + \frac{dv}{dy} \lambda \right)$$

Therefore the net transfer of momentum per unit area of the layer A per second

$$= \frac{m\,n\,\bar{c}}{6}\left\{\left(v + \frac{dv}{dy}\lambda\right) - \left(v - \frac{dv}{dy}\lambda\right)\right\}$$

$$= \tfrac{1}{3}\,m\,n\,\bar{c}\,\frac{dv}{dy}\,\lambda \qquad \ldots (4)$$

In the steady state of flow of the gas, this transfer of momentum is equal to the tangential viscous force $T = \eta\dfrac{dv}{dy}$.

Hence $\qquad \eta = \tfrac{1}{3}\,m\,n\,\bar{c}\,\lambda \qquad \ldots (5)$

Since $\qquad mn = \rho$, the density of the gas,

$$\eta = \tfrac{1}{3}\,\rho\,\bar{c}\,\lambda \qquad \ldots (6)$$

Using relation (6), the mean free path λ can be estimated. For, $\bar{c}$ can be calculated, when the density, pressure and temperature of the gas are given and the viscosity of the gas η can be experimentally determined.

Note : 1. Since $\bar{c}$ is proportional to $\sqrt{T}$, where T is the absolute temperature, $\eta \propto \sqrt{T}$, *i.e., the coefficient of viscosity of a gas varies directly as the square root of the absolute temperature of the gas.*

2. The density ρ of a gas increases with pressure, but the mean free path λ decreases in the same ratio, so that $\rho\lambda$ remains constant. In other words, if the pressure is halved, there are only half as many carriers of momenta, but each carry its momentum twice as far, since the mean free path is doubled. So the rate of transference of momentum is unaltered. Hence *the coefficient of viscosity is independent of pressure* at a given temperature.

3. Substituting for $\lambda = \dfrac{1}{\pi\sigma^2 n}$, relation (5) becomes

$$\eta = \tfrac{1}{3}\,m\,n\,\bar{c} \times \frac{1}{\pi\sigma^2 n}$$

$$= \frac{m\,\bar{c}}{3\pi\sigma^2} \qquad \ldots (7)$$

Hence the mass of the molecule m or the molecular diameter σ can be estimated, when the one or the other is known ; m can be readily calculated from the molecular weight M and the Avogadro's number N, since $m = M/N$.

Relation (7) also shows that η is independent of pressure or density, since n, which is dependent on pressure or density, does not appear in it. η is dependent only on the mass and diameter of the molecule and on the temperature.

In the following table, the molecular diameters and the mean free paths at N.T.P. of some gases are given :—

Gas	σ	λ
Hydrogen	$2{\cdot}47 \times 10^{-8}$ cm.	$1{\cdot}83 \times 10^{-5}$ cm.
Helium	$2{\cdot}18 \times 10^{-8}$,,	$2{\cdot}85 \times 10^{-5}$ cm.
Nitrogen	$3{\cdot}50 \times 10^{-8}$,,	$0{\cdot}944 \times 10^{-5}$ cm.
Oxygen	$3{\cdot}39 \times 10^{-8}$,,	$0{\cdot}995 \times 10^{-5}$ cm.

Example. Find the mean free path, frequency of collision and the molecular diameter of nitrogen gas, given $\eta = 166 \times 10^{-6}$ dyne per sq. cm. per unit velocity gradient, $\bar{c} = 4{\cdot}5 \times 10^{4}$ cms. sec.$^{-1}$ and $\rho = 1{\cdot}25 \times 10^{-3}$ gm. per c.c.

From (6), $\lambda = \dfrac{3\eta}{\rho\bar{c}} = \dfrac{3 \times 166 \times 10^{-6}}{1{\cdot}25 \times 10^{-3} \times 4{\cdot}5 \times 10^{4}} = 9 \times 10^{-6}$ cm.

Frequency of collisions $= \dfrac{\bar{c}}{\lambda} = \dfrac{4{\cdot}5 \times 10^{4}}{9 \times 10^{-6}} = 5 \times 10^{9}$

Assuming $n = 2{\cdot}7 \times 10^{19}$ per c.c. and using Maxwell's relation

$$\lambda = \frac{1}{\sqrt{2}\,\pi\,\sigma^{2}\,n},$$

$$\sigma = \left(\frac{1}{\sqrt{2}\,\pi\,n\,\lambda}\right)^{\frac{1}{2}}$$

$$= \left(\frac{1}{\sqrt{2} \times \frac{22}{7} \times 2{\cdot}7 \times 10^{19} \times 9 \times 10^{-6}}\right)$$

$$= 3 \times 10^{-8} \text{ cm.}$$

These values give an idea of the magnitudes of the quantities involved in the kinetic theory of gases.

Distribution of velocity among the molecules—Maxwell's law. In deriving an expression for the pressure of a gas, we tacitly assumed first that the number of molecules with a given velocity always remains the same and secondly that the velocity of a molecule changes only by impacts with the walls of the containing vessel. These two assumptions, however, cannot be true to facts, since the velocity of any individual molecule must be continually changing due to its collision with others. But, since we were concerned only with the mean square velocity and mean kinetic energy which always remain the same at the same temperature, no errors were introduced in the results obtained.

Maxwell, analysing the distribution of velocities of the molecules by the *statistical method,* was able to justify the above stated assumptions.

The statistical method is based on a very great number of active elements and leads to very satisfactory results when applied to systems made up of a very large number of elements, the precision obtained depending on the number of elements considered. Let us take an example. Every one knows that life insurance companies are based on statistics which gives how many men die per year. Experience shows that under determined conditions, in a population of several million inhabitants, the number of yearly deaths varies little, provided these conditions are not modified in a radical manner from one year to another. Supposing that out of a million policy holders, there is an average annual death rate of 3 per thousand or 3,000 per year, the company will calculate its rates so as to be able not only to meet its obligations, but also to pay a dividend to its share holders. The accuracy of this calculation is demonstrated by the fact that the company makes a profit, except in the case of war, epidemics, etc. It is readily seen that this accuracy and the profits, which are derived thereform, depend on the *number* of people insured. If there were only 10 policy holders, all living in the same house and if 9 were killed by an epidemic, the company would be bankrupt. When 100 policy holders are distributed in ten different houses, the chances of the company are greater, for it is unlikely that an epidemic will make all the hundred die. If there are 10 million policy holders, the chances of the company become almost a certitude.

From this consideration it follows also that the statistical method involves the application of the *laws of chance or probability* and hence the statistical laws are also called the laws of probability. The *probability* of an event is usually defined as *the ratio of the number of cases favourable to the event to the total number of possible cases,* all of these being considered equally probable. Without entering into the rather complicated calculus of probabilities, let us illustrate the general nature of probability by a simple example of the game of heads or tails. We know that if we toss a coin (which is ordinarily symmetrical, *i.e.*, not lopsided) a great number of times, we will obtain an equal number of heads and tails. The number of possible cases is evidently 2 (heads or tails) ; the two cases are equally probable ; therefore, when the coin is thrown up in the air the *probability* that it will come down heads (or tails) *is equal to 1* (number of cases favourable to each player) *divided by 2, or* ½. At the end of ten throws which have brought tails, the chance that the next throw will again bring tails are the *same* as after the first throw and the same holds good for the heads, *i.e.*, the probability is still ½. That is why, even if it is possible to win or lose in a game of chance, it is mathematically certain that if one plays *long enough*, the winnings and losses will balance themselves, on condition that the game is honestly played, that *chance alone* intervenes.

Applying the laws of chance or calculus of probabilities to the problem at hand, we shall now see how we are able to obtain remarkably precise results. A gas is constituted of a very large number ($2{\cdot}7 \times 10^{19}$ per c.c. at N.T.P.) of free molecules in perpetual motion. These molecules moving at different speeds, haphazardly, in all directions, impinge against each other and against the wall of the containing vessel. What we call *pressure of the gas* is nothing but the result of these impacts, the sum of the individual energies of each molecule stopped in its path by the walls of the vessel. The number of impacts per unit area of the surface per second will be the same, *on an average*, on every part of the walls, which means that the pressure is the same everywhere. Experience has verified this fact, which shows that the collisions are really the result of chance ; otherwise the pressure would be higher or lower at different points.

We know that one square cm. of the wall does not receive exactly the same number of impacts per second. But the energy of each individual collision is so slight with respect to the immense number of encounters, that the differences are too small to be detected. It is evident that a thousand impacts more or less, per unit area of the surface, introduces an error much too small to be measured by the most sensitive instruments which hardly register differences millions of times greater.

It is also evident that it is impossible to solve the problem by following the paths of the individual molecules. In other words, if we tried to solve the problem rigorously, without having recourse to a statistical method, we would have to write $2{\cdot}7 \times 10^{19}$ differential equations (20 followed by 18 zeros), each composed of $2{\cdot}7 \times 10^{19}$ terms representing the reciprocal actions of these molecules on one another. To solve such a problem it would take twenty billion human lives, assuming that each computer would only spend one second in dealing with each molecule. This is clearly impossible and enables one to understand why statistical methods based on the law of probability are absolutely necessary.

Hence, Maxwell, legitimately applying such a method to the case of a gas consisting of an assemblage of a very large number of molecules having velocity lying between zero and infinity, deduced the following expression for the number of molecules dn possessing velocities beween c and $c + dc$:—

$$dn = 4\pi \, n \, a^3 \, e^{-bc^3} \, c^2 \, dc \qquad \ldots (1)$$

where n is the number of molecules per c.c., and

$$a = \sqrt{b/\pi} = \sqrt{m/2\pi kT}.$$

Relation (1) is known as the *Maxwell's law of distribution of velocities.* It gives not the velocity of any individual molecule, but the probability that its velocity lies between c and $c + dc$ as :

$$4\pi \, a^3 \, e^{-bc^2} \, c^2 \, dc \qquad \ldots (2)$$

Thus the distribution law gives a knowledge of the gas only in a statistical sense.

It can now be proved that in a gas at a constant temperature, whatever the distribution initially, the gas will quickly reach a steady state in which the number of molecules possessing velocities between c and c + dc and hence moving with a given velocity c (dc being negligibly small) is constant. Putting $bc^2 = x^2$, relation (1) becomes

$$dn = 4n \, \pi^{-\frac{1}{2}} \, x^2 \, e^{-x^2} \, dx$$

which helps to represent the law graphically.

Plotting $y = 4\pi^{-\frac{1}{2}} \, e^{-x^2} \, x^2$ against x the curve obtained is of the form shown in Fig. 149. The number dn of the molecules whose velocities lie between x and $x + dx$ is proportional to the shaded area. The total area between the curve and the X-axis gives the total number n of the molecules having velocities between zero and infinity. The ordinate y corresponding to any value of x gives the number of molecules having a velocity represented by that value of x. It is also seen from the curve that the probability corresponding to $x = 1$

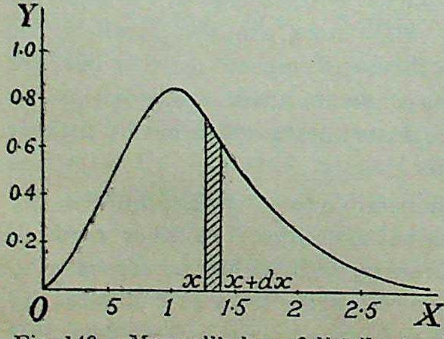


Fig. 149. Maxwell's law of distribution of velocities.

is greatest while it is considerably less for $x = \frac{1}{2}$ or 2. Hence we may conclude that the whole gas may be considered as endowed with the most probable velocity corresponding to $x = 1$.

This most probable velocity α is that value of c for which the number of molecules N_c with velocity c is a maximum. It may be estimated as follows :—

The mean square velocity C^2 is given by

$$C^2 = \frac{1}{n}\int_0^\infty c^2 \,.\, dn = \frac{3k\mathrm{T}}{m} \qquad \ldots(3)$$

which we have already obtained (*Cf.* p. 349).

The mean velocity $\bar{c}$ is given by

$$\bar{c} = \frac{1}{n}\int_0^\infty c \,.\, dn = \sqrt{\frac{8k\mathrm{T}}{\pi m}} \qquad \ldots(4)$$

$$\therefore \quad \frac{\bar{c}}{\mathrm{C}} = \sqrt{\frac{8}{2\pi}} = \cdot 921 \text{ or } \bar{c} = \cdot 921\mathrm{C}$$

The most probable velocity α is obtained by differentiating $y = 4\ \pi^{-\frac{1}{2}}\ e^{-x^2}\ x^2$ and equating it to zero $\left(i.e., \frac{dN_c}{dc} = 0\right)$. Substituting for N_c in the expression thus obtained, we get

$$\alpha = \sqrt{\frac{2k\mathrm{T}}{m}} = \sqrt{\frac{2}{3}}\ \mathrm{C}$$

Thus the most probable velocity α is less than the mean velocity $\bar{c}$, which itself is slightly less than root mean square velocity C. It is found that

$$\alpha^2 : \bar{c}^2 : \mathrm{C}^2 :: 1 : 1{\cdot}27 : 1{\cdot}5$$

Thus Maxwell's law establishes that in a steady state the number of molecules with a given velocity is constant even for a small volume of the gas. This does not mean that it is always the same molecules which are moving with a given velocity, but if some molecules change their velocity due to collisions, an equal number of other molecules acquire the initial velocity of the molecules which have now changed, so that the effect is the same as if the original molecules had continued to move with their initial velocity.

Maxwell's law of distribution of velocities was put to experimental test and found to be true. This experimental verification was done under very different circumstances, for instance (*i*) in connection with the study of the *Brownian movement* in colloidal solutions by Perrin, and (*ii*) in connection with the study of the *width of spectral* *lines* as applied to the *visibility of interference fringes* by Fabry and Buisson.

Maxwell's law of equipartition of energy—Relation between the kinetic energy of the molecules and the temperature of the gas. When two different gases at different temperatures are mixed together, it is observed that when the mixture reaches a steady state there is equalisation of temperature. Maxwell, analysing this experimental fact on the basis of the kinetic theory was able to show that the difference between the average kinetic energies of two sets of molecules tends to decrease with every collision and hence when the mixture of two gases reaches the *steady state of same temperature their molecules will have the same mean kinetic energy*, which means the equalisation of the kinetic energy of the molecules corresponds to equalisation of temperature, so that the kinetic energy of the molecules of a gas can be considered as an adequate measure of the temperature of the gas. This is known as *Maxwell's law of equipartition of energy*, which can be established as follows :—

Let m_1 be the mass of a molecule of one gas and m_2 a similar quantity for the other gas. When the two gases are mixed together, let these two molecules collide against each other. Let us consider the effect of this collision which is assumed to be perfectly elastic.

If u_1 and u_2 be the velocities of the two molecules before impact and v_1 and v_2 their velocities after impact along the line of impact, the momenta and kinetic energies before and after impact are related as :—

$$m_1u_1 + m_2u_2 = m_1v_1 + m_2v_2 \qquad \ldots(1)$$

$$\tfrac{1}{2}\, m_1u_1^2 + \tfrac{1}{2}\, m_2u_2^2 = \tfrac{1}{2}\, m_1v_1^2 + \tfrac{1}{2}\, m_2v_2^2 \qquad \ldots(2)$$

From equation (1),

$$v_1 = u_1 + \frac{m_2}{m_1}\,(u_2 - v_2)$$

Substituting this in equation (2) and solving the latter, we get

$$v_2 = \frac{2m_1u_1 + (m_2 - m_1)\,u_2}{(m_1 + m_2)}$$

and
$$v_1 = \frac{2m_2u_2 + (m_1 - m_2)\,u_1}{(m_1 + m_2)}$$

Using these values of v_1 aud v_2, the difference of kinetic energies of the two molecules after impact

$$= \tfrac{1}{2}\, m_1v_1^2 - \tfrac{1}{2}\, m_2v_2^2$$

$$= (\tfrac{1}{2}\, m_2 u_2^2 - \tfrac{1}{2}\, m_1 u_1^2) \left\{ \frac{8 m_1 m_2}{(m_1 + m_2)^2} - 1 \right\}$$

$$+ \frac{4 m_1 m_2\, (m_1 - m_2)\, u_1 u_2}{(m_1 + m_2)^2} \qquad \dots (3)$$

Relation (3) refers to a single collision of a single pair of molecules. In the actual case of the mixture of the two gases, there will be an exceedingly large number of the two kinds of molecules and a large number of such collisions, and what we are interested in is the total collision effect, or the average statistical effect of the mutual collisions of the very large number of molecules. It does not appear from the above equation whether the difference in the kinetic energies of the two molecules has increased or decreased due to the collision. We can, however, arrive at more definite conclusions as regards the effect upon the gases in bulk.

The second term, *viz.*,

$$\frac{4 m_1 m_2\, (m_1 - m_2)\, u_1 u_2}{(m_1 + m_2)^2}$$

will be the same for every collision, but for the factor $u_1 u_2$. If we consider all the cases in which u_1 and u_2 have given magnitudes, there will be just as many cases where they have the same sign as those where they have the opposite sign ; hence adding all these together the total statistical effect due to this term will be zero.

Considering the first term, *viz.*,

$$(\tfrac{1}{2}\, m_2 u_2^2 - \tfrac{1}{2}\, m_1 u_1^2) \left\{ \frac{8 m_1 m_2}{(m_1 + m_2)^2} - 1 \right\}$$

we see that the difference in the kinetic energies will increase or decrease due to the collision, according as the absolute value of the factor

$$\left\{ \frac{8 m_1 m_2}{(m_1 + m_2)^2} - 1 \right\}$$

is greater or less than unity. Assuming that

$$\left\{ \frac{8 m_1 m_2}{(m_1 + m_2)^2} - 1 \right\} < 1$$

or $$\frac{8 m_1 m_2}{(m_1 + m_2)^2} < 2 \text{ or } \frac{4 m_1 m_2}{(m_1 + m_2)^2} < 1$$

or $$4 m_1 m_2 < (m_1 + m_2)^2$$

i.e., $0 < (m_1 - m_2)^2$, which is true unless $m_1 = m_2$, since $(m_1 - m_2)^2$ is always a positive quantity being a square, whether

m_1 or m_2 be greater. Hence the assumption made above is correct, which means the difference between the kinetic energies of the two sets of molecules after impact is less than the difference between the kinetic energies before impact. Or, more generally stated, the difference between the average kinetic energies of two sets of molecules tends to decrease with every collision.

From this we conclude that when two gases at different temperatures are mixed, the great number of collisions between the molecules of the two gases will reduce the difference between the average kinetic energies of the two sets of molecules to zero, *i.e.*, the kinetic energies will be equalised. Now from experimental observation we know that when two gases are mixed equalisation of temperature occurs. Further, we have seen that the temperature of a gas is proportional to the mean kinetic energy of the molecules. Hence two gases must be at the same temperature when their molecules have the same mean kinetic energy, so that the temperature of a gas is measured by the mean kinetic energy of its molecules.

Atomicity of gases. One of the fundamental assumptions of the kinetic theory is that the molecules are homogeneous, perfectly elastic spheres. This means that when two molecules collide the sum of their kinetic energies of translation is unaltered by the collision. Such an assumption is valid in the case of the monatomic gases, for which the only form the kinetic energy can assume is that of *translation* of the molecule. The same cannot be said of polyatomic gases, *i.e.*, those which contain two or more atoms in the molecule. For, it is quite probable in their case that the atoms in the molecule are *vibrating* with respect to one another and the whole molecule may be *rotating* about one or more axes. There will be both kinetic and potential energies associated with those motions which might be referred to as the *internal energy* of the molecule.

It is evident that there will be an exchange between the translational kinetic energy and the internal energy of the molecules at every collision and hence the former need not be conserved. In a state of equilibrium for any temperature and for a definite kind of molecule, the total kinetic energy is divided into the three components, translation, vibration and rotation, and there is a definite ratio between the average values of the kinetic energy of translation and the internal energy of vibration and rotation. We shall see later how the ratio of the total energy to the translation energy of the molecules throws light on the atomicity of the gas.

But it is to be borne in mind that the translational kinetic energy is conserved on the average, since the results obtained on this assumption are true for all gases, monatomic and polyatomic. This is due to the fact that considering a very large number of collisions made by a given molecule, the amount of translational energy converted into internal energy is equal to that of internal energy converted into translational energy, so that on the whole the translational energy is conserved.

Degrees of freedom and their application to equipartition of energy—Boltzmann's law. Boltzmann investigated more thoroughly Maxwell's law of equipartition of energy and enunciated it in a more rigorous form, based on a more general conception known as the *degrees of freedom.*

L. Boltzmann

The number of degrees of freedom of an object is the number of facts which must be specified in order to describe completely its state or position. For instance, the position of a point in space is determined by the three axes X, Y and Z of the Cartesian coordinate system. Three is the smallest number of coordinates which can define the position of the point. Similarly two points are specified by six coordinates. Applying this to a dynamical system where a body is in motion, if the body is a point, it can have at most three degrees of translational motion. If the body were to be with a finite size and rigid, it can not only move, but also rotate about an axis passing through it. Since this rotatory motion can be resolved, like the translatory motion, into components about any three mutually perpendicular axes through a point fixed in it, a rigid body will have three more degrees of freedom of rotational motion. Hence to completely describe the state of motion of a rigid body six coordinates are required. The degrees of freedom may, therefore, be defined as *the total number of coordinates required to specify completely the position and configuration of any dynamical system.*

We have seen above that two points in space are completely defined by six coordinates. But, if there is some definite relation between the two points, the number of coordinates necessary for a complete description is reduced by one, so that a system of these two points is said to have only five degrees of freedom. Including this aspect, the number of degrees of freedom is actually equal to *the total number of coordinates required to define the positions of the elements of the system minus the number of independent relations existing between the elements.* Hence, if the number of atoms in a molecule of a gas is x, the number of degrees of freedom cannot exceed $3x$; for a monatomic gas, $x = 1$, so that its degrees of freedom will be 3; for a diatomic gas having two atoms at a fixed distance apart, the number of degrees of freedom will be $(3 \times 2 - 1) = 5$; for a triatomic gas, we may have two different arrangements of the atoms: either a central atom with the two others placed on either side of it or the three atoms at the apices of a triangle. The number of degrees of freedom in the first case is equal to $(3 \times 3 - 2)$ or 7, and in the second case $(3 \times 3 - 3)$ or 6. In this manner one may calculate the number of degrees of freedom of any polyatomic molecule; the number of degrees of freedom will increase, in general, with the complexity, unless other factors interfere.

Law of equipartition of energy according to the degrees of freedom. According to Maxwell's theory of equipartition of energy, in the steady state

$$\bar{u}^2 = \bar{v}^2 = \bar{w}^2$$

where $\bar{u}$, $\bar{v}$ and $\bar{w}$ are the average values of the component velocities of a molecule.

$$\therefore \qquad \tfrac{1}{2} m\bar{u}^2 = \tfrac{1}{2} m\bar{v}^2 = \tfrac{1}{2} m\bar{w}^2 = \tfrac{1}{3} \cdot \tfrac{1}{2} m\mathrm{C}^2$$

$$\text{But} \qquad \tfrac{1}{2} m\mathrm{C}^2 = \tfrac{3}{2} k\mathrm{T} \qquad (Cf.\ \text{p. } 349)$$

and the three components refer to the three coordinate axes and hence give the number of degrees of freedom.

$\therefore$ The *mean kinetic energy per molecule per degree of freedom* $= \frac{1}{3} \cdot \frac{3}{2} k\mathrm{T} = \frac{1}{2} k\mathrm{T}$.

This result is true for any number of degrees of freedom and is known as the *law of equipartition of energy in the different degrees of freedom.* It states that *for any dynamical system in thermal equilibrium the total energy is divided equally among all the degrees of freedom and the energy associated with one molecule per degree freedom =* $\frac{1}{2} k\mathrm{T}$ *and hence a constant.*

The mean kinetic energy per gram molecule per degree freedom = $\frac{1}{2}k\text{T} \times \text{N} = \frac{1}{2}\text{RT}$, where N is the Avogardo's number and R the gas constant for a gram molecule.

We can now continue with the application of the kinetic theory to other thermal phenomena such as specific heat and conductivity.

Specific heats of gases. The specific heats of gases can be readily calculated on the basis of Maxwell's law of equipartition of energy and Boltzmann's theorem of the degrees of freedom. According to the former, the temperature of a gas is measured by the mean kinetic energy of the molecules and the molecules of different gases at the same temperature possess the same mean kinetic energy. According to the latter, the mean kinetic energy is equally divided between the degrees of freedom, corresponding to translation, vibration and rotation.

Taking, first, a *monatomic gas*, its molecules can have only the motion of translation, no vibration or rotation. Hence heat communicated to such a gas at constant volume can only increase the kinetic energy of translation. According to the theory of equipartition of energy, this energy of translation will be equally divided among the *three* translational degrees of freedom.

The total energy U of 1 gram molecule of the gas at the absolute temperature T is given by

$$\text{U} = 3 \times \tfrac{1}{2}k\,\text{T} \times \text{N} = \tfrac{3}{2}\,\text{RT} \qquad \dots (1)$$

(where N is the Avogardo's number, R the gas constant per gram molecule), since the energy per molecule per degree freedom = $\frac{1}{2}k\text{T}$ (*Cf.* p. 366).

If C_v is the molecular specific heat *at constant volume, i.e.*, the quantity of heat required to raise one gram molecule through one degree, then

$$\text{C}_v = \frac{d\text{U}}{d\text{T}} = \tfrac{3}{2}\,\text{R} \qquad \dots (2)$$

Taking $\text{R} = 8{\cdot}32 \times 10^7$ ergs, and $\text{J} = 4{\cdot}186 \times 10^7$ ergs per calorie

$$\text{C}_v = \frac{3 \times 8{\cdot}32 \times 10^7}{2}\text{ ergs} = \frac{3 \times 8{\cdot}32 \times 10^7}{2 \times 4{\cdot}186 \times 10^7}\text{ cals.}$$

$$= 2{\cdot}98 \text{ calories.}$$

If C_p is the molecular specific heat *at constant pressure*, since $\text{C}_p - \text{C}_v = \text{R}$ (*Cf.* p. 141),

$$\text{C}_p = \text{C}_v + \text{R} = \tfrac{5}{2}\,\text{R} \qquad \dots (3)$$

$$= 4{\cdot}96 \text{ calories.}$$

From relations (2) and (3), it is seen that the molecular specific heats C_v and C_p of monatomic gases are constants, *independent of the temperature and the nature of the gas.* These predictions agree with experimental results : Thus for argon $C_v = 2{\cdot}97$ at all temperatures. Other substances examined, such as vapours of mercury and zinc and the other inert gases like helium, neon, krypton, which are monatomic, $C_v = 3$ over a wide range of temperature.

For *diatomic gases*, remembering that they have in all five degrees of freedom, three translational and two rotational, the total energy is given by

$$U = \tfrac{5}{2} RT$$

$$\text{Hence} \qquad C_v = \tfrac{5}{2} R \text{ and } C_p = \tfrac{7}{2} R \qquad \ldots (4)$$

$$\therefore \qquad C_v = 4{\cdot}96 \text{ calories, } C_p = 6{\cdot}94 \text{ calories.}$$

These theoretical conclusions agree on the whole with experimental results for a large number of diatomic gases, such as hydrogen, oxygen, nitrogen, CO, NO, etc., which have for C_v sensibly the same value equal to 5 calories about. But theory predicts here also independence of C_v on the temperature and nature of the gas, which is not satisfactorily verified by experiments. Thus, at low temperatures C_v falls to $\frac{3}{2} R = 2{\cdot}98$ calories, as Eucken's experiments on hydrogen show, indicating thereby that the rotation has disappeared. Similarly for the halogens (Cl_2, Br_2, I_2) C_v is greater than $\frac{3}{2}$ R varying from 6 to 6·5, indicating that the two atoms may not be rigidly fixed but vibrate along the line of centres. As already indicated, the variation of the specific heat with temperature is satisfactorily explained by the quantum theory (*Cf*. Chapter III, p. 164).

In *triatomic gases*, the atoms may be arranged in two different ways with the corresponding 6 or 7 degrees of freedom as already mentioned. In the former case $C_v = 6 \times \frac{1}{2} R = 3R$ and $C_p = 4R$; in the latter $C_v = \frac{7}{2} R$ and $C_p = \frac{9}{2} R$. In *polyatomic gases*, we should, therefore, expect C_v to be equal to or greater than 6 calories. Such, indeed, is found to be the case with water vapour and methane. More often, the value found is considerably greater, *e.g.*, 8 for acetylene, 10 for CS_2, 15 for chloroform. Since the probability of internal modification as a result of collision might be expected to be higher the more complex the molecule, these high values are not to be wondered at. It is to be noted that it is not possible to calculate in a simple manner the energy of internal vibration of such complex molecules since the vibrations are not freely and fully developed.

Note : Specific heat of solids. The atomic heat of solid elements also can be calculated in a similar manner by the application of equipartition of energy and degrees of freedom. We can consider the atoms of a solid element as elastic spheres held in position by the attraction of other atoms and capable of vibrating in a simple harmonic manner about a mean position of equilibrium. The atom will have *three* degrees of freedom of vibrational motion and the kinetic energy associated with each degree of freedom is $\frac{1}{2}kT$. Further, it can be shown that the average kinetic energy during an oscillation is equal to the average potential energy. Hence the total energy associated with each degree of freedom is kT.

Therefore the total energy U of one gram-atom of the solid at an absolute temperature T is given by

$$U = 3kT \times N = 3RT$$

$$\therefore \text{ The atomic heat } C_v = \frac{dU}{dT} = 3R = 5{\cdot}96 \text{ calories.}$$

The atomic heat of all solid elements is thus about 6 calories, which agrees with Dulong and Petit's empirical law. But according to the kinetic theory, the atomic heat is independent of temperature, which is not experimentally verified, particularly at very low temperatures, where the value shows a marked decrease. Further, the decrease is gradual and cannot be explained by the disappearance of any degree of freedom involving discontinuous changes by multiples of $\frac{1}{2}R$. One cannot assume fractional degrees of freedom. Here the principles of classical dynamics and the equipartition law of the kinetic theory fail completely. The quantum theory has been able to explain more satisfactorily experimental data, as already indicated in Chapter III (*Cf.* p. p. 127-8).

Ratio of the specific heats of gases. Since this quantity is given by the relation

$$\gamma = \frac{C_p}{C_v},$$

$$\text{for } \textit{monatomic gases}, \; \gamma = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1{\cdot}66,$$

$$\text{for } \textit{diatomic gases}, \; \gamma = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1{\cdot}40,$$

$$\left.\begin{array}{l} \text{for } \textit{triatomic gases}, \; \gamma = \dfrac{4R}{3R} = \dfrac{4}{3} = 1{\cdot}33, \\ \qquad\qquad\qquad \text{or } \gamma = \dfrac{\frac{9}{2}R}{\frac{7}{2}R} = \dfrac{9}{7} = 1{\cdot}28. \end{array}\right\}$$

For more complex molecules, γ approaches unity but is always greater than unity, since $C_p > C_v$.

These theoretical conclusions agree with experimental results for all the monatomic gases and for a large number of diatomic and polyatomic gases studied. It is to be noted that the determination of γ combined with the kinetic theory gives valuable information about the constitution of the molecules of gases.

Note : The ratio of the total energy to the translational energy of the molecules, which we have mentioned in connection with the atomicity of gases, throws light on the distribution of energy according to the constitution of the molecules. For, if unit mass of a gas is heated through a rise of temperature $d\mathrm{T}$, the increase in total energy is $C_v \,.\, d\mathrm{T}$, and the increase in translational energy is $\frac{3}{2}\mathrm{R} \,.\, d\mathrm{T}$.

Hence $$\frac{\text{increase in total energy}}{\text{increase in translational energy}} = \alpha = \frac{C_v \,.\, d\mathrm{T}}{\frac{3}{2}\mathrm{R} \,.\, d\mathrm{T}}$$

$$\therefore \qquad \alpha = \tfrac{2}{3} \cdot \frac{C_v}{\mathrm{R}} = \tfrac{2}{3} \cdot \frac{C_v}{C_p - C_v} = \tfrac{2}{3} \cdot \frac{1}{\gamma - 1} \quad \ldots(1)$$

Several gases, such as mercury vapour and the inert gases have for γ the value of $\frac{5}{3}$, as we have shown above. For these gases therefore,

$$\alpha = \tfrac{2}{3} \times \frac{1}{\frac{2}{3}} = 1,$$

which means that the total energy is equal to the translational energy. Hence the molecules of these gases possess no internal energy, or the internal energy does not change with temperature. This indicates that the molecules are monatomic, which has helped to solve the difficult problem of finding the atomic weights of the inert gases. The ordinary methods cannot be employed, since these gases do not enter into chemical combination. But since the above consideration shows that they are monatomic, their atomic weights must be the same as the molecular weights, which can be determined by the vapour density method.

Diatomic gases have for γ the value 1·4 or $\frac{7}{5}$, Substituting this value in (1)

$$\alpha = \tfrac{2}{3} \times \frac{1}{\frac{2}{5}} = \tfrac{5}{3}.$$

This shows that the internal energy of the molecules in diatomic gases is two-thirds of the translational energy.

Since the greater the atomicity of the gas the nearer the value of γ approaches unity, the greater is the value of α in relation (1). This means that the more complex the molecule, the internal energy becomes much geater as compared to the translational energy.

Thermal conductivity of gases. The thermal conductivity of gases is explained by the kinetic theory in precisely the same way as in the case of the viscosity of gases (*Cf.* p. 356) except for this difference that the molecules are considered in the present problem as carriers of heat energy instead of momentum. Hence an expression for the conductivity of a gas can be derived by a reasoning similar to that used for viscosity.

Between the hot and cold ends, the gas is considered to be composed of a great number of molecular layers, the molecules of one layer differing from those of another only in having a different temperature. Further in the steady state, the temperature will decrease at a uniform rate as one proceeds from the hot to the cold end, *i e.*, a uniform temperature gradient is assumed. Under these conditions, there will be a net transfer of heat due to the kinetic motion of the molecules.

Considering a layer A at a distance y from the cold end OX, let the temperature be θ and temperature gradient $\frac{d\theta}{dy}$ (Fig. 150).

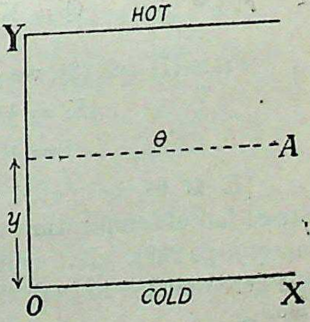


Fig. 150.

The molecules which cross the layer A from above will have a greater kinetic energy than those from below. Also, among the molecules which move towards A, only those which on the average are not farther away than the mean free path λ will cross it, so that we may assume that the mean temperature of the molecules crossing from below is $\left(\theta - \frac{d\theta}{dy}\lambda\right)$ and of those from above $\left(\theta + \frac{d\theta}{dy}\lambda\right)$.

Hence total heat carried by all the molecules moving *downwards* and crossing the layer A per unit area per second

$$= \frac{m\,n\,\bar{c}}{6}\,C_v\left(\theta + \frac{d\theta}{dy}\lambda\right),$$

and total heat carried by all the molecules moving *upwards* and crossing A per unit area per second

$$= \frac{m\,n\,\bar{c}}{6}\,C_v\left(\theta - \frac{d\theta}{dy}\,\lambda\right)$$

where m is the mass of the molecule, n the number of molecules per c.c., $\bar{c}$ the average velocity of the molecules, so that $n\,\bar{c}/6$ is the number of molecules crossing A downwards or upwards per unit area per second (*Cf.* p. 355) and C_v the specific heat of the gas at constant volume, so that

$$m\,C_v\left(\theta + \frac{d\theta}{dy}\,\lambda\right) \text{ and } m\,C_v\left(\theta - \frac{d\theta}{dy}\,\lambda\right)$$

represent the heat carried by *one* molecule across A downwards and upwards respectively.

Therefore the net transfer of heat per unit area of A per second will be

$$Q = \frac{m\,n\,\bar{c}}{6}\,C_v\left\{\left(\theta + \frac{d\theta}{dy}\,\lambda\right) - \left(\theta - \frac{d\theta}{dy}\,\lambda\right)\right\}$$

$$= \tfrac{1}{3}\,m\,n\,\bar{c}\,C_v\,\lambda\,\frac{d\theta}{dy} \qquad \dots (1)$$

The thermal conductivity K of the gas is defined as the quantity of heat that flows per unit area per unit time per unit temperature gradient and is given by the relation

$$Q = K\,\frac{d\theta}{dy} \qquad \dots (2)$$

From (1) and (2), we get

$$K = \tfrac{1}{3}\,m\,n\,\bar{c}\,C_v\,\lambda \qquad \dots (3)$$

$$= \tfrac{1}{3}\,\rho\,\bar{c}\,C_v\,\lambda \qquad \dots (4)$$

[It is to be noted that $d\theta/dy$ is $-$ve, since it represents the rate of fall of temperature with distance in the direction of the heat flow (*Cf*. p. 238). But as it appears in both the relations (1) and (2) it is here omitted in both the places.]

Comparing relation (4) with a similar relation for the coefficient of viscosity; *viz*,, $\eta = \frac{1}{3}\,\rho\,\bar{c}\,\lambda$ (*Cf*. p. 356), we get

$$K = \eta\,C_v \qquad \dots (5)$$

This relation is true only if all the heat supplied is converted into kinetic energy of translation. Hence it is usual to express it, in general, as

$$K = A\,\eta\,C_v \qquad \dots (6)$$

The coefficient A, as calculated by Chapman and Enskog, should be approximately equal to 2·5 for monatomic gases, 1·9 for diatomic gases, 1·75 for triatomic gases, and still less for higher polyatomic gases. Experiment appears to confirm these predictions in a very satisfactory manner. The kinetic theory of gases thus predicts the existence of a remarkably simple relation between K, η and C_v.

Since, in relation (4), the variation of C_v is small, the *thermal conductivity,* like viscosity, *varies directly as the square root of the absolute temperature* ($\bar{c} \propto \sqrt{T}$) *and is independent of pressure* ($\rho\lambda$ = constant). *Cf.* p. 356

At *low* pressures, however, both the viscosity and the thermal conductivity of gases are proportional to pressure, which forms the principle of some low-pressure gauges. The kinetic theory has been able to explain also the behaviour of gases at low pressures very satisfactorily on the basis that the mean free path becomes very large so that the velocity or temperature gradient can no longer be assumed as continuous.

Experimental confirmation of the kinetic theory. The basic concept on which the kinetic theory is built is *motion of molecules due to thermal agitation,* a motion so rapid and so irregular, which still leaves the gas in bulk motionless. Although the various thermal and allied phenomena, which receive an adequate explanation on the principles of kinetic theory, may be considered as experimental evidence of the validity of the theory, yet they are still only *indirect proofs*, since the various assumptions of the kinetic theory have been introduced more or less empirically based on them. This leaves the desirability of having independent and direct experimental confirmation of the above mentioned fundamental postulate of the proposed theory. As already mentioned, there exist two such evidences, *viz.*, the *Brownian movement* and the *width of spectral lines*, the former being more direct than the latter. We shall, therefore, briefly describe these two phenomena and show how they adequately verify the kinetic theory.

Brownian movement. If very fine particles in suspension in a liquid are observed under a powerful microscope, they are found to be moving rapidly and incessantly in an irregular fashion in all directions. Each particle spins, rises, sinks and rises again without ever coming to rest ; the smaller the particle the more lively and noticeable are its movements. The movements continue indefinitely without showing any signs of stopping or even abating ; they are independent of the nature of the suspended particles, particles of the same weight and size being equally agitated, independent of the nature of the liquid, although more lively the less viscous the liquid, and independent of the uniformity of temperature. The phenomenon has been named the *Brownian movement* after the English botanist, Brown, who first discovered it in 1827.

It was at first thought that the Brownian movement was due to surface tension, irregularities in the temperature of the liquid, chemical action, and so on. All these explanations were found inadequate and the phenomenon remained unexplained for nearly fifty years, until it was realised that it was due to the motion of thermal agitation of the molecules of the liquid. The irregularity of the motion of the particles points clearly to a similar irregularity in those of the molecules of the liquid. It is easily understood that the forces due to molecular impact will almost completly balance if the size of the particle is very large, so that the Brownian movement cannot be observed with large sized particles. But if the particle is sufficiently small, it will be acted upon by a resultant unbalanced force and will consequently move in a random fashion corresponding to the haphazard movement of the molecules of the liquid ; the smaller the particle, the larger and the more irregular the movements will be as is experimentally observed. Thus we have a direct evidence of the motion of the molecules due to thermal agitation which forms the basic postulate of the kinetic theory, and a visible demonstration of the validity of the kinetic theory even in the case of liquids.

Einstein succeeded in formulating a quantitative theory for the Brownian movement which can be put to experimental tests. Perrin carefully carried out these tests, using colloidal solutions in which fine granules were suspended and was able to verify not only the haphazard and incessant molecular motion due to thermal agitation but also Maxwell's law of distribution of velocities governing such motion. As a final and crucial test, he determined the Avogadro's number N from his experimental data and found the value agree very well with that obtained by entirely different methods.

Width of spectral lines and visibility of interference fringes. This phenomenon verifies Maxwell's law of distribution of velocities among the molecules of a gas, in motion due to thermal agitation, though in a less direct manner than the Brownian movement.

Michaelson with his interferometer using radiations emitted by the particles of a luminous gas contained in a Geissler tube obtained concentric circular interference fringes. Analysing the visibility of these fringes he came to the following conclusions :—If the radiation is perfectly monochromatic, *i.e.*, of one particular wavelength, the fringes are always clear and visible ; but in the case of non-homogeneous radiation, the visibility of the fringes varies according to the path difference of the interfering beams, fringes appearing and disappearing as the path difference is increased steadily. Now the non-homogeneity of the radiation may arise due to several causes : for instance, if the source emits composite light or in the case of a single and pure gas due to increase of pressure. But the case which is of special interest to our present purpose is the creation of non-homogeneity by the movement of the molecules of the gas which occurs at all pressures and broadens spectral lines. Under these circumstances, the phenomenon of the visibility of interference fringes will take place and from its study one might be able to verify Maxwell's law of distribution as the molecular motion is the chief cause for such an event.

Lord Rayleigh studied the phenomenon quantitatively. Applying first Doppler's effect, he was able to account for the width of spectral lines. Considering next the visibility of the interference fringes, he arrived at a theoretical formula, giving the limiting order of interference, *i.e.*, the order of interference for which the fringes just disappeared, $p = 2d/\lambda_0$ where d is the path difference of the interfering beams whose mean wavelength is λ_0. Supposing that all the molecules of the gas emitting the radiations had the same mean velocity, he obtained an expression for p, as

$$p = 1{\cdot}03 \times 10^6 \sqrt{M/T}$$

where M is the molecular weight of the gas and T the absolute temperature.

But supposing that the molecules moved subject to Maxwell's law, it is found that $p = 1{\cdot}42 \times 10^6 \sqrt{M/T}$, taking the condition of visibility $a = 1/40$.

Fabry and Buissón verified this relation, experimentally by measuring the path difference d necessary for the fringes to disappear starting from perfect visibility. They got for p ($= 2d/\lambda_0$) the value $1{\cdot}22 \times 10^6 \sqrt{M/T}$ using the condition of visibility a as equal to 1/16 and not 1/40, which is justified since visibility to some extent is subjective. The experimental result was thus found to agree with the theoretical value. Studying different gases at different temperatures they were also able to confirm the two theoretical predictions, *viz.*, the limiting order of interference p varies directly as the square root of the molecular weight of the gas and inversely as the square root of the absolute temperature. Thus, Maxwell's law governing the motion of the molecules of a gas in thermal equilibrium was experimentally confirmed, though in an indirect manner.

QUESTIONS

1. Discuss the caloric theory of heat and give a critical survey of the evidence which led to its downfall and substitution by the dynamical theory.

2. Describe a laboratory method of determining J. Give experimental details. (*Delhi University 1951*)

3. Describe with relevant theory Rowland's method of finding the mechanical equivalent of heat. Point out the significance of the result. (*Madras University ; Nagpur University 1956*)

4. The height of the Niagara Falls is 50 metres. Calculate the difference in temperature of the water at the top and bottom of the Fall if $J = 4{\cdot}2 \times 10^7$ ergs/cal. **Ans.** 0.1165°C. (*Punjab University 1953*)

5. Describe Callendar and Barnes' continuous flow method of measuring the mechanical equivalent of heat. State how the method can be adopted to measure the variation of specific heat of water between 10°C and 90°C. (*Punjab University 1951 ; Allahabad University 1951 ; Madras University*)

6. Given that the mean radius of the earth is 6400 km., and its mean specific heat is 0·15, find the rise in temperature of the earth, if the energy of rotation is suddenly transformed to heat. **Ans.** 68·76°C. (*Madras University*)

7. In an experiment using Callendar and Barnes' continuous flow method the p.d. across the wire was 3 volts and the current 2 amperes ; the rise in temperature of the water 2·7°C and the rate of flow of water 30 gms. per minute. When the rate of flow was increased to 48 gms. per minute, the p.d. to 3·75 volts and the current to 2·5 amperes, the rise in temperature of the water was the same as before. Calculate the value of J. **Ans.** $4{\cdot}167 \times 10^7$ ergs/cal. (*Punjab University 1951*)

8. The specific heat of helium at constant pressure is 1·25. Assuming the gas to be monatomic, calculate the mehanical equivalent of heat. One litre of the gas at N.T.P. weighs 0·1785 gm. **Ans.** $4{\cdot}125 \times 10^7$ ergs./cal. (*Madras University*)

9. Give the outlines of the methods by which the mechanical equivalent of heat can be determined. Assuming that for air at constant pressure the coefficient of expansion is 1/273, the density at 0°C and atmospheric pressure is 0·001293, the specific heat $C_p = 0{\cdot}2389$ and the ratio $C_p/C_v = 1{\cdot}405$, calculate the mechanical equivalent of heat. Suppose that there is inappreciable cohesion between the molecules. **Ans.** $4{\cdot}16 \times 10^7$ ergs./cal. (*Bombay University*)

10. A lead bullet at a temperature of 47·6°C strikes against an obstacle. If the heat produced by the sudden stoppage is sufficient to melt the bullet,

with what velocity the bullet strikes the obstacle ? It is assumed that all the heat goes to the bullet. Melting point of lead = 327°C, specific heat of lead = ·03 cal. /gm./degree, latent heat of fusion of lead = 6 cals./gm., $J = 4{\cdot}2 \times 10^7$ ergs/cal. **Ans.** $3{\cdot}475 \times 10^4$ cms./sec. (*Utkal University 1950*)

11. Give a critical account of the methods available for determining the mechanical equivalent of heat.

In the absence of bearing friction a winding engine could raise a cage weighing 1000 kg. at 10 metres per sec., but this is reduced by friction to 9 metres per sec. How much oil initially at 20°C is required per sec. to keep the temperature of the bearing down to 70°C ? (Sp. heat of oil = 0·5 ; $g = 981$ cms./sec.^{2} ; $J = 4{\cdot}2 \times 10^7$ ergs/cal.) **Ans.** 93·4 gms.

12. Outline the essential features of the kinetic theory of gases. Find an expression for the pressure of a gas on the basis of the kinetic theory.

(*Punjab University 1954, 1955, 1957 ; Madras University ; Delhi University 1954*)

13. Outline the essential features of the kinetic theory of gases and apply it, so far as you can, to account for the laws of Boyle, Avogadro and Charles.

(*London B.Sc.*)

14. Give an account of the simple kinetic theory of gases and deduce a value of the mean square of the molecular velocity. Explain how Boyle's law follows from this theory. (*Tripos Part I*)

15. Show that the general properties of the three states of matter are accounted by the kinetic theory. Deduce the equation of a perfect gas.

(*Punjab University 1952*)

16. Show that the pressure exerted by a perfect gas is $\frac{2}{3}$ of the kinetic energy of the molecules in a unit volume. Explain on the basis of the kinetic theory (*i*) why the temperature of a gas rises when it is compressed, and (*ii*) why the temperature of an evaporating liquid is lower than its surroundings.

(*Punjab University 1956*)

17. Deduce an expression for the pressure of a gas from the assumptions of the kinetic theory. Point out clearly the fundamental hypothesis you adopt.

Find the square root of the mean square of the velocity of the molecules of nitrogen at 20°C. Molecular weight of nitrogen is 28, the gas constant R for a gram molecule is $8{\cdot}315 \times 10^7$ ergs per degree centigrade.

Ans. $5{\cdot}11 \times 10^4$ cms./sec. (*Tripos Part I*)

18. The density of helium is 0·178 gm. per litre at N.T.P. What is the R.M.S. velocity of helium molecules under these conditions ? Compare it with the velocity as 200°C. **Ans.** $1{\cdot}306 \times 10^5$ cms./sec. ; 1 : 1·316.

(*Madras University*)

19. Distinguish between the average velocity, most frequent velocity, "root-mean-square" velocity of the molecules of a gas.

Calculate the root-mean-square velocity of the molecules of hydrogen and of a gas of molecular weight *m* at 0°C and 100°C from the following data : Density of hydrogen at N.T.P. = 0·0000896 gm. per c.c. ; density of mercury = 13·6 gms. per c.c. **Ans.** $1{\cdot}84 \times 10^5$ cms./sec., $2{\cdot}15 \times 10^5$ cms./sec.

$\frac{2{\cdot}60 \times 10^5}{\sqrt{m}}$ cms./sec., $\frac{3{\cdot}02 \times 10^5}{\sqrt{m}}$ cms./sec. (*London B.Sc.*)

20. What is the meaning of *mean free path* of the molecules of a gas. Show that it is equal to $1/\pi n d^2$ where n is the number of molecules per c.c., and d the diameter of each molecule. Show that the mean free path is proportional to pressure. (*Bombay University 1947*)

21. On the basis of the kinetic theory deduce an expression for the viscosity of a gas in terms of the mean free path of its molecules. Show that it is independent of pressure but depends upon the temperature of the gas. (*Baroda University 1954*)

22. Mention the evidence in support of molecular agitation. How does the kinetic theory enable us to calculate theoretically the ratio of specific heats of mono and diatomic gases ? (*Madras University*)

23. Find an expression for the energy of a gas on the kinetic theory of gases and calculate the ratio of the specific heats for monatomic and diatomic gases. (*R. University 1949*)

24. Outline the essential features of the kinetic theory of gases and apply it to account for the simple gas laws. What is the interpretation of temperature on this theory ?
(*Punjab University 1955 ; Utkal University 1955 ; Allahabad University 1945*)

25. Explain what is meant by the "mean square velocity" of the molecules of a gas and their "mean free path". Show how these two quantities can be found. (*Bombay University 1924*)

26. Show that the pressure of a gas is equal to two-thirds of the kinetic energy of translation per unit volume. Calculate the kinetic energy of hydrogen per gram molecule at 0°C. (*Allahabad University 1949*)

27. Deduce an expression for the thermal conductivity of a gas from the kinetic theory. How would you actually proceed to determine the conductivity of any particular gas. (*Allahabad University B.Sc. Hons. 1931*)

28. State the law of equipartition of energy. Prove that for a monatomic gas the ratio between the specific heats is 5/3 and for a diatomic gas it is 7/5. (*Allahabad University 1932*)

29. Investigate the relation between the coefficient of thermal conductivity (K) and viscosity (η) of a gas and show that $K = \eta C_v$ where C_v is the specific heat at constant volume. (*Madras University B.Sc. Hons.*)

30. Write notes on :—
- (*i*) Brownian movement
- (*ii*) Visibility of interference fringes
- (*iii*) Degrees of freedom
- (*iv*) Maxwell's law of distribution of molecular velocities.

CHAPTER VII

LOW TEMPERATURE—LIQUEFACTION OF GASES

Introduction. For a long time the idea that nothing could be colder than ice was prevalent and hence the temperature of ice was chosen as the lowest point of the scale in the early designs of thermometry. Fahrenheit was the first to demonstrate clearly the existence of temperatures much lower than that of ice by placing a mercury thermometer in a mixture of ice and common salt when the mercury thread went right down to − 18°C. He, therefore, chose this temperature as the zero of the scale which goes by his name. But we now know that much lower temperatures than even the Fahrenheit's zero exist. Study of the gas laws shows that the lowest temperature attainable, at least theoretically, is 273°C below the melting point of ice, which is used as the zero of the absolute scale of thermometry. With further and continued researches in different problems encountered in the phenomena produced by heat, great advances have been made in a practical way towards the absolute zero, which has now been well nigh reached. In this chapter we shall describe how all this has been done. We shall first deal with the principles and devices employed in reaching lower and lower temperatures right up to the absolute zero (*production of low temperature*), then with the means of detection of such low temperatures (*measurement of low temperature*) and finally with some important uses of low temperature (*practical applications of low temperature*).

PRODUCTION OF LOW TEMPERATURES

The general principle involved in the production of low temperature is to devise means for removing from a body its heat content. The following methods have been employed, with what results we shall presently see.

(*i*) *Freezing mixtures* of salts in ice.

(*ii*) *Cooling due to evaporation* of liquids under reduced pressure.

(*iii*) *Liquefaction of gases* by cooling them sufficiently and simultaneously subjecting them to a large pressure.

(*iv*) *Cooling due to Peltier effect, i.e.*, by suitably applying an external *e.m.f.* to a thermocouple, one of the junctions can be cooled.

(*v*) *Cooling due to desorption.* Charcoal absorbs residual gases and when these gases escape at still lower pressure, cooling results due to the *heat of adsorption*, by a process similar to the evaporation of liquids.

(*vi*) *Adiabatic demagnetisation, i.e.*, by demagnetising certain crystals adiabatically, magnetic energy is made to leave the system and thereby extreme cooling is produced under suitable conditions.

Of these methods, the first two, *viz.*, freezing mixtures and cooling by evaporation are of practical importance, as they are utilised in the modern refrigerating machines. The third one, based on liquefaction of gases, is the most important, since it is intimately connected with the production of very low temperatures and is of great interest on account of the theoretical principles involved as well of the many practical applications both in science and industry. The fourth method based on Peltier effect has not yet been successfully exploited and hence nothing will be said about it. The method of cooling due to desorption has its use in aiding to a further cooling of an already very much cooled system. For example, charcoal absorbs helium gas at 5 atmospheres and 10°K and the subsequent desorption to 0·1 mm. pressure lowers the temperature to 4°K which is sufficient to liquefy helium. The last method of adiabatic demagnetisation is of special interest to the physicist, as it has enabled him to reach almost the absolute zero, where matter, so to say, is born, and any information concerning the nature of substances in that region is bound to be of great value. It is to be noted that most of these methods are not exclusive of each other but complementary, in the sense that they can be used conjunctively to reach the desired low temperature. We have given above an example to substantiate this statement in the case of cooling due to desorption and we shall meet with more such cases below.

Freezing mixtures. A simple and easy method of production of temperatures much lower than that of ice is *by adding suitable salts to ice.* When a salt, say NaCl, which is above 0°C, and ice are mixed, some of the ice melts in cooling the salt down to its own temperature and a saturated solution of salt at 0°C is produced. But ice cannot remain in equilibrium with a saturated solution of salt at 0°C any more than with hot water. Hence the ice melts taking the necessary latent heat from the solution, which in consequence cools down. The cooling of the solution goes on up to about −22°C, at which temperature the ice attains equilibrium with the saturated solution. The cooling process is also helped by the heat of solution, *i.e.*, the heat absorbed when salt dissolves in water. This is the *principle of freezing mixtures*.

We have already mentioned that the behaviour of freezing mixtures is very similar to that of alloys with the formation of a *cryohydrate* at the lowest temperature called the *eutectic point*. (*Cf.* p. 177). Hence the low temperature produced by different salts will be different, depending on the composition of the eutectic mixture as well as on the different values of their heats of solution. The table below illustrates these points.

Salt	*Amount in 100 grams of mixture*	*Minimum temperature (eutectic) in °C*
$MgSO_4$	19·0 gms.	— 3·9
$ZnSO_4$	27·4 ,,	— 6·5
KCl	19·7 ,,	—11·1
NH_4Cl	18·6 ,,	—15·8
$NaNO_3$	37·0 ,,	—18·5
NaCl	22·4 ,,	—21·2
$MgCl_2$	21·6 ,,	—33 6
$CaCl_2$	29 8 ,,	—55·0

It is seen that a suitable mixture of ice and calcium chloride produces as low a temperature as —55°C ; the cooling is found to be pretty rapid due to the large negative heat of solution of calcium chloride.

Cooling due to evaporation at reduced pressure. Low temperature may also be produced by *allowing suitable liquids to evaporate at reduced pressure*. When a liquid evaporates it requires latent heat of vaporisation. If the evaporation is made to take place rapidly by some contrivance and if the liquid is isolated, the latent heat of vaporisation is obtained at the expense of the heat content of the liquid itself and intense cooling results.

The oldest apparatus based on this principle is *Wollaston's cryophorus* shown in Fig. 151. It consists of a bent tube with a bulb at each end. One of them (A) contains water or some other more volatile liquid. The rest of the apparatus is exhausted before it is sealed off, so that the whole space above the liquid is filled with the vapour of the liquid. When the other bulb (B) is immersed in a freezing mixture, the vapour in it condenses and the pressure of the vapour in A is reduced so much that the liquid in A evaporates rapidly. The latent heat required for this purpose is taken from the rest of the liquid itself since the evaporation is so rapid that the liquid cannot get that heat fast enough from the surroundings. In consequence the liquid freezes.

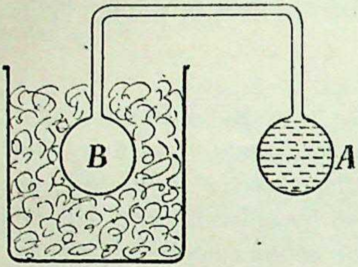


Fig. 151. Wollaston's cryophorus.

The modern refrigerator used for industrial and domestic purposes is built on this principle. Water is not a suitable liquid to use in a refrigerator although it has high latent heat of evaporation, since its vapour pressure at low temperatures is small. The liquids commonly employed are ammonia and sulphur dioxide. The main types of refrigerator will be described more in detail later.

Liquefaction of gases. With the early acquisition of the knowledge that steam could be liquefied either by cooling or by increase of pressure, a general belief was entertained that substances which are gaseous at ordinary temperatures could be liquefied if they were sufficiently cooled and subjected simultaneously to a large pressure. While cooling reduced the heat motion of the molecules, applied high pressure made the molecules come sufficiently close together to coalesce and form a liquid. If the liquid so cooled were allowed further to evaporate rapidly, still lower temperatures could be obtained.

But practical attempts soon showed that the problem of liquefaction of gases was not as easy as all that ; new fields had to be explored and more precise knowledge had to be first gained concerning the behaviour of gases over a wide range of temperatures and pressures, before gases could be liquefied and thus made to serve the purpose of production of low temperatures. This subject is a good illustration of how progress in science is made by a coordinated teamwork in the fields of both theory and practice. As a matter of fact, the century-long adventure in this special branch started with the liquefaction of chlorine by Faraday in 1823 and terminated with the solidification of helium by Keesom in 1926, with several important researches by many other scientists, which contributed to the steady advance of the work.

Investigations on the behaviour of gases. The progressive tackling of the problem may be divided into four stages :—

In the **first stage** *attempts were made based on the general idea of cooling a gas as much as possible and at the same time applying a large pressure,* with the vague hope that if the gas happened to get below a sufficiently low temperature it would be liquefied. Faraday's experiments are illustrative of this stage.

Faraday's experiments. Faraday's apparatus, shown in Fig. 152, is extremely simple. Some substance from which chlorine is liberated, such as manganese dioxide and hydrochloric acid or chlorine hydrate, is placed in a V-shaped stout glass tube, which is then sealed off. The sealed end is immersed in a freezing mixture. On heating the end which contains the chlorine compound, a large amount of chlorine gas is produced which collects at the other end in the freezing mixture and finally liquefies under its own pressure into a yellow liquid. This was the first instance of liquefying a substance which was thought to be a real gas. Faraday also succeeded to liquefy nitrous oxide, carbon dioxide and cyanogen by the same process. But gases like oxygen, nitrogen, hydrogen and carbon monoxide could not be thus liquefied, even when extremely high pressures were applied. Faraday termed them *permanent* gases.

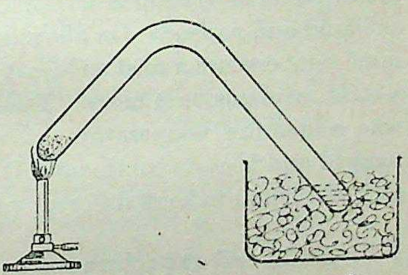


Fig. 152. Faraday's apparatus for liquefaction of chlorine.

The **second stage** *consists in the discovery of the critical temperature,* first by Cagniard de la Tour in a general way and then more precisely by Andrews from his researches on carbon dioxide.

Cagniard de la Tour's experiment. Cagniard de la Tour, in 1862, was studying the effect of heating various liquids, such as water, alcohol, etc., in a closed vessel under the pressure of their own vapour. His apparatus consisted of a bent sealed tube, one end A of which contained the experimental liquid, the other end B air, the interspace being occupied by a column of mercury (Fig. 153). The arrangement was placed in an oil-bath and heated. As the temperature rose, the liquid vaporised to keep up with the increased saturation vapour pressure but no boiling could take place, since the liquid was always under the pressure of its own saturated vapour; but the mercury column was pushed up in the other limb, compressing the air in B. After a time, it was noticed that the meniscus of the liquid gradually flattened and at a certain temperature, lost its curvature altogether and disappeared, the contents of the end A becoming homogeneous, undistinguishable as liquid and vapour. On allowing the bath to cool, at nearly the same temperature a mist suddenly appeared and disappeared, leaving a faint meniscus once more. These observations showed that there was a definite temperature at which the liquid and vapour states merged and became continuous. It was called the *critical temperature* and was found to have different values for different substances.

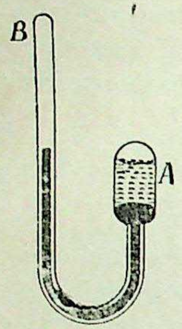


Fig. 153. Cagniard de la Tour's apparatus.

Andrews' experiments on carbon dioxide. Study of the properties of vapours clearly indicated that deviation from the gas laws was intimately connected with the process of liquefaction of a gaseous substance, as the deviation became more marked when the gas was nearing liquefaction. Bearing this in mind, Andrews, in order to determine the exact conditions required to liquefy a gas, undertook, in 1869, *study of the isothermals of carbon dioxide* at different temperatures.

The *principle* involved in these experiments is to measure the volume of a fixed mass of the gas at various pressures at a given constant temperature and draw the curve relating the pressure and volume, which is called an *isothermal*. Obtaining in a similar manner the isothermals for different fixed temperatures within the range to be investigated, it is possible to see when and how the gas deviates from Boyle's law.

The apparatus used by Andrews in obtaining the isothermals for carbon dioxide is shown in Fig. 154. Two similar glass tubes A and B, whose top portions are thick-walled capillary of uniform bore, middle parts rather wide and bottom portions of decent bore, are employed. The capillary parts are carefully calibrated using a thread of mercury, while the tubes are still open at both the ends. In one of the tubes (A) carbon dioxide is enclosed while in the other (B) air by the following procedure. A stream of pure and dry carbon dioxide is passed through A over a long period (24 hours) to remove all traces of air, and then the tube is sealed at both ends. The lower end is opened after immersing it under mercury and a small pellet of mercury M is drawn in by heating and subsequent cooling, so that CO_2 is enclosed in the space above M. Air is enclosed in B in a similar manner. A and B are firmly fixed in two strong copper cylinders CC, with the capillary parts alone projecting outside. The cylinders are provided with screw plungers SS at the bottom. Filling the cylinders with water and screwing in the plungers the water is compressed and the pressure is transmitted to the enclosed gases. Pressures of the order of 400 atmospheres can thus be applied. By establishing communication between the cylinders through a cross-tube D, both the enclosed gases will always be subjected to the same pressure. The capillary parts jutting out of the pressure cylinders are surrounded by two water baths, the one round the air tube being kept at a constant temperature, while the other enclosing the carbon dioxide tube being maintained at any desired temperature between 0° and 100°C.

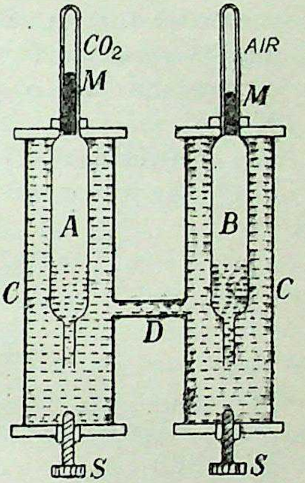


Fig. 154. Andrews' apparatus.

The plungers are screwed in until the mercury pellets in the two tubes appear above the cylinders, which occurs at about 30 atmospheres. The volume of each gas is directly read since the tubes are calibrated and from that of the air, its pressure and hence that of the carbon dioxide can be calculated, since they are subjected to the same pressure, assuming air to obey Boyle's law. These observations are made for different values of the pressure applied until the smallest volume which can be accurately measured is reached. The experiment is repeated maintaining the carbon dioxide tube at different temperatures. From the data thus obtained isothermal curves connecting the pressure and volume of the enclosed carbon dioxide at various temperatures can be obtained, which are of the form shown in Fig. 155.

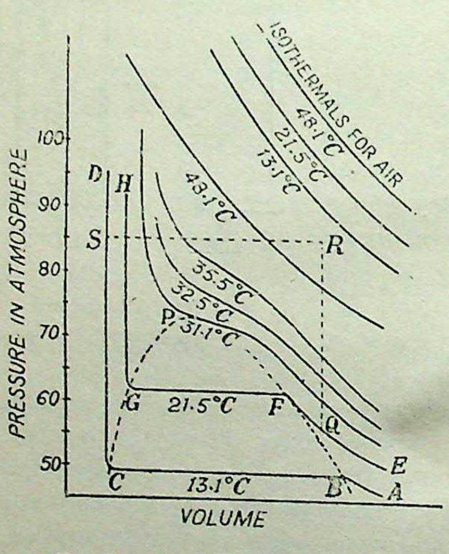


Fig. 155. Isothermals of carbon dioxide.

Considering the lowest of these curves, *viz.*, the isothermal at 13·1°C, the portion AB represents the behaviour of carbon dioxide while it is still a gas, obeying Boyle's law roughly even up to B, the point of saturation. It is found to be more compressible in this region than that allowed by Boyle's law, which means that pv decreases as p increases. The horizontal portion BC of the curve corresponds to the change of the gas into liquid, where the saturation pressure remains constant while the volume is decreasing. At C all the gas is liquefied and after that the curve becomes practically vertical (portion CD) since the liquid is almost incompressible. The next curve, *viz.*, the isothermal EFGH at 21·5°C exhibits similar characteristics, with the following differences, however, *viz.* (*i*) the horizontal portion is shorter, which means that there is less difference between the volumes of the saturated vapour and of the liquid, *i e.*, the density of the liquid and that of the vapour are approaching one another and (*ii*) the starting point G of the vertical part of the curve is at a higher pressure indicating that a larger pressure is required to liquefy the gas at the higher temperature, which means, in its turn, that the compressibility of the liquid is approaching that of the gas. Turning our attention to the isothermal at 31·1°C, the horizontal portion, corresponding to the discontinuous change from the gas to the liquid state, has disappeared, indicating thereby that the gas cannot be liquefied any longer and that its volume diminishes regularly with increase of pressure, but much faster than would be expected if the gas obeyed Boyle's law. Isothermals at 32·5°C and 35·5°C show the same tendencies, although the portion of abnormally large compressibility is becoming less marked and at 48·1°C it has disappeared completely and the isothermal has become similar to that of a permanent gas, as can be seen from the isothermals for air given on the top of the same figure for comparison.

Andrews found that the highest temperature at which any noticeable liquefaction occurred and whose isothermal showed a horizontal portion was 30·9°C. This then was the *critical temperature*, where the properties of a liquid and its saturated vapour coincide, in confirmation of the finding of Cagniard de la Tour. The isothermal corresponding to that temperature is known as the *critical isothermal.* The dotted curve, shown in Fig. 155, joining the extremities of the horizontal parts of the isothermals touches the critical isothermal at a point of inflexion P known as the *critical point.* To the right of the dotted curve the substance is unsaturated vapour, within the curve it is a mixture of saturated vapour and liquid and to its left it is entirely in the liquid state. The pressure and volume coordinates of P are the *critical pressure* and *critical volume* of the substance. The critical temperature T_c, the critical pressure p_c and the critical volume v_c are known as the *critical constants* of a gas and may be defined as follows :—

The *critical temperature* of a gas is that temperature, below which alone the gas can be liquefied by mere increase of pressure and above which the properties of the liquid and gaseous states are indistinguishable or, in other words, the gas cannot be liquefied by any amount of pressure.

The *critical pressure* is the pressure that should be applied to a gas at its critical temperature in order to liquefy it.

The *critical volume* is the specific volume of a gas under conditions of critical temperature and pressure

The results of Andrews' experiments may be summed up as follows :—

(*a*) There is *no essential difference between liquefiable and permanent gases.* Any gas can be liquefied below its critical temperature. Carbon dioxide remote from its critical temperature behaves like the permanent gases, oxygen, nitrogen, hydrogen, etc. These are simply substances which at room temperature are much above their critical temperatures and hence cannot be liquefied by the mere application of pressure, as seen from the values of their critical temperature :— oxygen (— 118·8°C), nitrogen (— 147·1°C), hydrogen (— 239·9°C).

(*b*) There exists a *continuity of state* between the gas and liquid phases of a substance, which can be visualised by the following consideration. Starting with a given mass of the substance in the state represented by the point Q (Fig. 155), where it is undoubtedly a gas, let it be heated at constant volume until the point R is reached and then let it be cooled at constant pressure until the point S is reached, where it is entirely liquid. At no point in the above mentioned operations in changing the substance from the gaseous to the liquid state has any discontinuity occurred. Andrews regarded the gas and liquid states as merely distant stages of a series of continuous physical changes, or as widely separated forms of the same condition of matter which can be made to pass from one to the other by a series of changes so graded that no breach of continuity happens. Thus at high temperatures and low pressures the substance approximates to the conditions of an ideal gas obeying Boyle's law. Increase of pressure and reduction of temperature make the substance deviate sensibly from Boyle's law, and acquire the properties of the liquid state, thereby losing gradually the distinctive properties of an ideal gas.

(*c*) *State of matter near the critical point.* Andrews put forward a simple and probably a correct view on this point by saying that just beyond the critical temperature the whole mass is converted into vapour consisting of a single constituent and should behave like a gas near its point of condensation. But Cailletet and Colardeau were of opinion that the liquid state persists even beyond the critical point, since, for example, iodine which dissolves in liquid CO_2 and not in gas CO_2, was found even beyond the critical point, to dissolve in CO_2. The properties of matter actually observed near the critical point appear to be in favour of Andrews' opinion. They are : (*i*) the densities of the liquid and the vapour gradually approach each other till they become equal at the critical point ; (*ii*) at the critical temperature the boundary line between the liquid and vapour disappears ; (*iii*) compressibility of vapour is very great near the critical point, becoming infinite at the point itself.

The experiments of Callendar seem, however, to throw fresh light on the state of matter near the critical point. Using very pure water from which all traces of dissolved air had been expelled, he found that the densities of liquid and vapour did not become equal at

374°C, the critical temperature at which the meniscus disappeared, but that a difference of density was perceptible even beyond the critical point which under favourable conditions could be traced up to 380°C. This seems to point to the existence of a *critical region* rather than a critical point. More research is needed for a final decision in this matter.

Experimental determination of the critical constants. The actual measurement of the critical constants is not easy. The critical temperature and pressure can be readily measured with fair accuracy by a method similar to that used by Cagniard de la Tour. A hard glass tube connected to a manometer may be employed. Sufficient quantity of the liquid is introduced into the tube. The tube is surrounded by a thermostat which can be maintained at constant temperatures differing by very small amounts. The temperatures at which the liquid suddenly disappears and reappears are noted, the mean of these giving the critical temperature. The critical pressure corresponding to that temperature can be obtained easily from the manometer.

The *measurement of critical volume* offers much greater difficulty because at the critical state, even for small variations of pressure the volume varies enormously. Moreover, in order to obtain a correct reading of the critical volume, it is necessary that the substance is exactly at the critical temperature. Even a small alteration, such as 0·1°C at or just below the critical point produces a considerable change in the volume and for this reason a small error in the temperature leads to a considerable error in the volume.

The most accurate method of measuring the critical volume is that devised by Cailletet and Mathias, based on mean densities or the *law of rectilinear diameters.* Experiments on the densities of a liquid and its vapour up to the critical point show that the density of the saturated vapour increases with temperature up to the critical point while that of the liquid decreases, and near the critical point the two approximate to equality. This behaviour was experimentally determined by Cailletet and Mathias. They measured the density ρ (which

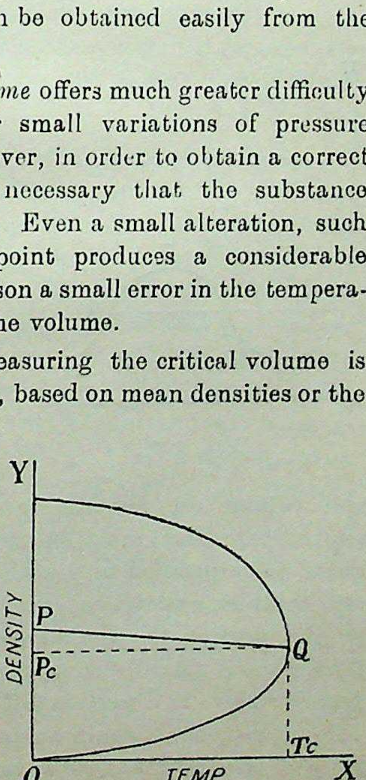


Fig. 156

is equal to $1/v$, v being the specific volume) of the liquid and its vapour at different temperatures in the vicinity of the critical temperature. Plotting the data, *i.e.*, density against temperature, a curve roughly parabolic, as shown in Fig. 156, is obtained. It is seen that the densities of the liquid and vapour go on approaching each other till they become equal at the critical temperature. PQ is nearly a straight line, representing $y = \frac{1}{2}(\rho_l + \rho_v)$, *i.e.*, passing through the points representing the mean of the densities of the liquid and vapour at different temperatures. It will naturally pass through the critical temperature, since the densities of the liquid and vapour are the same there; hence the point Q where this line, called the rectilinear diameter, intersects the two curves is the critical temperature T_c and the ordinate of Q is the density ρ_c at the critical point, from which the critical volume can be found, since $v_c = 1/\rho_c$.

James Thomson's hypothesis. Prof. J. Thomson supplemented the idea of continuity, so much insisted upon by Andrews, by an ingenious speculation concerning the isothermals below the critical temperature. He suggested that the horizontal part BC which made the curve sharply discontinuous at B and C should be replaced by a continuous curve BEFGC, so that the whole isothermal would be continuous throughout (Fig. 157). He further pointed out that with such a modification certain phenomena such as supercooling and superheating could be easily explained. In the part BE the substance must evidently be in an unstable state since its pressure and volume are not the same as on the straight portion BC; the temperature also must be greater, although it should be actually lower, corresponding to the whole isothermal. Hence *the portion BE represents an unstable supercooled state* of the substance. Similarly in the portion CG, the temperature of the substance must be lower than what it actually is; hence CG *would represent the unstable superheated state.* The portion GE, where the pressure increases with the volume, represents again an unstable condition, which might *represent the phenomenon of boiling by bumping*, but which is not easily conceived, nor ever realised in a homogeneous mass. It has been found that a

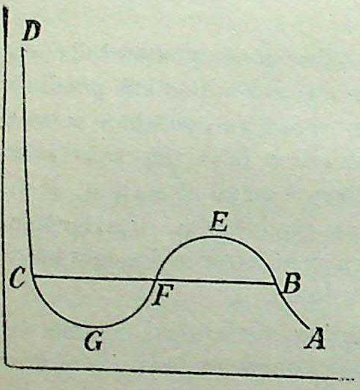


Fig. 157.

curve obeying van der Waals' equation must generally be of this shape (*Cf.* below). Maxwell has pointed out that if Thomson's suggestion is to be admitted, the shape of the curve must be such that the area of BEF is equal to that of CGF.

The **third stage** *in the investigation of liquefaction of gases is marked by a detailed investigation of the isothermals of the permanent gases over a wide range of temperature and pressure,* in order to fully establish that there is no essential difference between the parmanent gases and those which have been liquefied.

The problem as to whether a gas obeys Boyle's law or not was tackled in the following manner. A gas that strictly obeys Boyle's law at all pressures, however high or low, is called a perfect or ideal gas. Hence for a given mass of a perfect gas at a given constant temperature, if the pressure p be plotted against the volume v the graph should be a rectangular hyperbola, or if the product pv be plotted against p, the graph should be a straight line parallel to the p-axis. Plotting the pv vs. p graphs in the case of actual gases it should be possible to study, by their departures from the straight line characteristics of the graph of a perfect gas, the nature of their deviations from Boyle's law.

Boyle had shown that in the range of pressures from about ·03 atmosphere to 4 atmospheres all the ordinary gases obeyed his law. Despretz, in 1827, extending the range up to 20 atmospheres, compressed equal volumes of different gases, like air, ammonia, carbon dioxide and hydrogen enclosed in similar barometer tubes kept side by side in the same cistern of mercury, and showed that the volumes occupied by the gases under the same pressure were not equal. Ammonia and carbon dioxide were more compressible than air while hydrogen was less compressible. This showed that at least some of the gases did not obey Boyle's law strictly. In 1847, Regnault, after a series of experiments on the behaviour of ordinary gases towards Boyle's law up to pressures of 30 atmospheres found that the pv vs. p -curves were not straight lines parallel to the p-axis but inclined to it, and pv diminished as p increased for all the gases except hydrogen, for which pv increased with p. Several other workers, like Natterer and Andrews,-carried out similar investigations and arrived at similar results. But the classical experiments of Amagat with pressures reaching up to 3,000 atmospheres have to be considered somewhat in detail.

Amagat's experiments. In 1880, Amagat carried out an exhaustive study of the behaviour of several gases employing a method where the high pressures were produced directly by a column of mercury of the necessary height and measured by finding its height. He used a steel tube about 1,000 ft. long fixed to a vertical shaft of a coal mine. The lower end of the tube was sealed into a mercury reservoir at the bottom of the mine. A carefully calibrated tube closed at the top and containing the experimental gas was put in communication with the mercury reservoir. High pressures were obtained by means of a large screw working in the mercury reservoir. The calibrated tube was surrounded by a bath, the temperature of which can be varied over a wide range. The behaviour of nitrogen for various pressures was first carefully investigated. In the study of other gases, a calibrated tube containing nitrogen was used for measuring the pressures. Thus the volume and temperature of any gas could be directly observed, while the pressure was determined by the nitrogen tube. Amagat's typical results are represented in Figs. 158, 159 and 160.

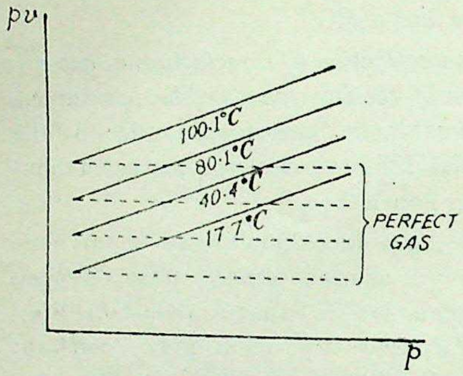


Fig. 158. Hydrogen.

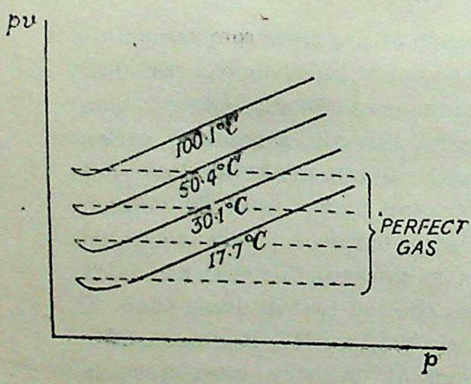


Fig. 159. Nitrogen.

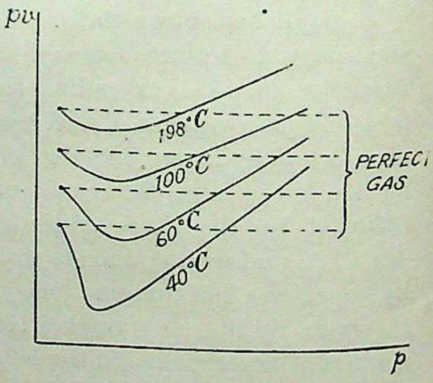


Fig. 160. Carbon dioxide.

An inspection of these figures shows that the gases examined may be classified into two categories. *Hydrogen (Fig. 158) is typical of the first class*, where *pv* increases steadily with pressure, as indicated by the straight line curves inclined upwards ; such gases are less compressible than would be expected from Boyle's law. This behaviour of hydrogen is found to be true even at such low temperatures as – 80°C. *Other gases, such as air, oxygen, nitrogen (Fig. 159), carbon dioxide (Fig 160), ethylene, etc., fall under the second class*, where *pv* first diminishes with increase of pressure to a minimum and then increases continuously with pressure. With the more easily liquefiable among them, like carbon-dioxide, the initial diminution of *pv* is more pronounced than in the case of the less easily liquefiable gases, like nitrogen.

It should be noted, however, that at higher pressures the curves of all gases become sensibly straight and parallel. Further, later investigations have shown that hydrogen also at sufficiently low temperatures (below – 175°C) behaves like all the other gases exhibiting an initial diminution of *pv* to a minimum value.

The results obtained by Amagat may be summarised as follows :—

(*i*) actual gases do not obey Boyle's law at high pressures ;

(*ii*) easily condensible gases show more marked deviations than permanent gases at the same temperature ;

(*iii*) deviations from Boyle's law are similar for all gases at different temperatures characteristic of each gas.

The *chief drawback of Amagat's method* consisted in the impossibility of accurate measurement of extremely small volumes of the gas at the highly compressed stages. To avoid this difficulty Holborn and his collaborators devised a method in which the volume of the gas was kept constant and the quantity of the gas was varied.

Holborn's experiments. In 1915, Holborn designed an apparatus, shown in Fig. 161, the special features of which are an *ingenious pressure balance* capable of measuring accurately very high pressures and a *special device for measuring the mass of the gas*, by allowing it to expand into a series of vessels of known volume until its pressure is about one atmosphere.

The *pressure balance*, shown on the right side of the figure, consists of a rigidly fixed metallic cylinder C with a central hole in which a metal rod R fits accurately like a piston. At the bottom of the hole a tube D is connected, through which the balance can be put in communication with that part of the apparatus which contains the experimental gas. The pressure of the gas is transmitted through oil contained in the space below R. The oil serves also the purpose of lubrication, so that R moves smoothly without friction in its socket. The force due to the pressure of the gas which tends to raise R is just prevented by the screw S pressing on the top of R with the combined weight of the frame F and the load W attached to the frame. To avoid any error due to non-uniformity of the cross-section of the socket, the piston is always in the same place when measurements are actually made. When balance is obtained the pressure of the gas $p = mg/a$, when m is the sum of the masses of R, S, F and W, and a the effective cross-section of the balance (*i.e.*, of the piston or its socket), which is found separately by means of open-air mercury manometer and is a constant from 1 to 100 atmospheres. In this range, the balance is capable of detecting a change in pressure of 1 mm. mercury or about ·001 atmosphere, hence very sensitive.

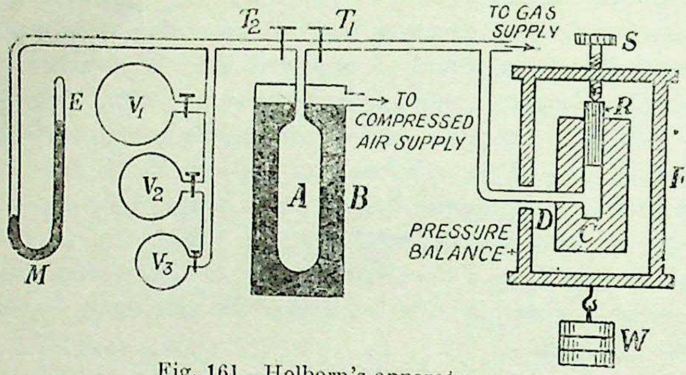


Fig. 161. Holborn's apparatus.

A stout glass cylindrical vessel A contains the gas under study and is enclosed in a steel cylinder B nearly full of mercury which is kept at the same pressure as the gas inside A by means of a supply of compressed air both for safety and to avoid correction for the expansion of A due to the pressure of the gas inside it. The whole of A and B is surrounded by a suitable bath (not shown in Fig.) which can be maintained constant at any desired temperature. A is provided with connecting tubes by means of which it can be put in communication with the pressure balance or with the device for measuring the mass of the gas, using the stop-cock T_1 or T_2. The special arrangement for measuring the mass of the gas consists of a set of twelve flasks with suitably graded known volumes, V_1, V_2, V_3 [illegible] each one provided with a tap. The flasks are surrounded by a constant temperature water bath (not shown in Fig.). A closed mercury manometer M, in which the space E is exhausted, is connected with the flasks.

In performing the experiment, the apparatus is first of all exhausted. Then with the stop-cock T_2 closed and T_1 open, the experimental gas is pumped into A until the required high pressure is attained, as measured by the pressure balance. Next closing the stop-cock T_1, and opening T_2, the gas is allowed to expand into the flasks V_1, V_2, V_3......, by opening the corresponding taps until the pressure is nearly equal to that of the atmosphere, as measured by the manometer M. Since the volumes of the vessel A and of the connecting tubes up to T_1 and T_2 have been accurately determined, the volume of the gas enclosed in A at a given temperature, as indicated by a thermometer immersed in the bath surrounding A and B, and a given pressure, as accurately measured by the pressure balance, is known. The mass of the gas is found as follows :—

Since the various flasks used for allowing the gas to expand in order to reduce its pressure and the connecting tubes have all been accurately calibrated, the volume of the expanded gas is given by the sum of the volumes of the vessel A, of the flasks actually used and of the connecting tubes ; its actual pressure is given by the manometer reading and its temperature by a thermometer immersed in the bath surrounding the flasks. From these data, the volume of the expanded gas at N.T.P. can be calculated, assuming legitimately that the perfect gas equation is obeyed, since the actual pressure and temperature of the gas differ now so little from the normal values. From the volume of the gas at N.T.P., its mass is calculated.

To repeat the experiment at a *different high pressure,* the lower-pressure side of the apparatus is exhausted and the stop cock T_2 is closed and the operations described above are gone through again and thus the desired range of pressure is covered. The whole process is repeated for different temperatures of the gas.

For studying the results obtained, since it is found convenient to plot pv against p, from the mass of the gas required to occupy a given volume at different pressures, actually measured in the experiment, the volume occupied by a fixed mass of the gas at the same pressures can be calculated.

Holborn and Schultz, Holborn and Otto and Kammerlingh Onnes have employed this method in determining the isothermals of a great number of gases over a considerable range of pressure and temperature. Holborn and Otto have investigated several gases up to 100 atmospheres and in the range from + 400°C to −183°C. Onnes has pushed the study to still lower temperatures.

Their results are usually represented by the following empirical relation, proposed by Holborn and Otto :—

$$pv = \mathrm{A} + \mathrm{B}p + \mathrm{C}p^2 + \mathrm{D}p^3 + \ldots$$

where A, B, C, etc. are constants characteristic of each gas, which vary with temperature ; they are termed *virial coefficients* and their values diminish rapidly as $\mathrm{A} \gg \mathrm{B} \gg \mathrm{C}$ and so on. The constant A is evidently equal to RT of the perfect gas equation. From this relation the following deductions can be made :—

At infinitely low pressures ($p \to 0$) all gases obey Boyle's law accurately. This conclusion is borne but by experimental observation and is utilised in the construction of *the perfect gas scale*, as already mentioned (*Cf.* p. 37).

At low pressures, all gases obey Boyle's law approximately, the deviations being negligibly small. Experimental data at low pressures are far from satisfactory. Amagat conducted a saries of very careful investigations on air, hydrogen, nitrogen and carbon dioxide at low pressures and was not able to detect any deviations from Boyle's law. Rayleigh confirmed Amagat's results by similar researches. But others, such as Bohr, Baly and Ramsay obtained results contrary to those of Amagat. Such contradictions are not surprising, on account of the great difficulties encountered in making accurate measurements at low pressure ; errors creep in due to possible condensation of the gas and occlusion of the gas into the walls of the apparatus.

As the pressure increases, more and more terms become necessary in the relation given above. Under these conditions, B is the most important term and it is found that it varies in a similar way for all gases, starting with a negative value at low temperatures and gradually increasing to zero at a particular temperature and then becoming positive. The particular temperature at which B = 0 is called the *Boyle temperature*, because the gas obeys Boyle's law for a considerable range of pressure at that temperature ; it is found that *the Boyle temperature is approximately 3 times the critical temperature of a gas ; hence different for different gases* ; it can be analytically expressed by

$$d\,(pv)/dp = \mathrm{B} = 0.$$

The results obtained can also be studied by plotting pv against p. The curves for carbon dioxide, shown in Fig. 162, are typical for all gases, the only adjustment being that the temperature of any particular isothermal is different for each gas, so that the Boyle temperature is different for different gases. This is the reason why the values of the temperature are not given on the curves.

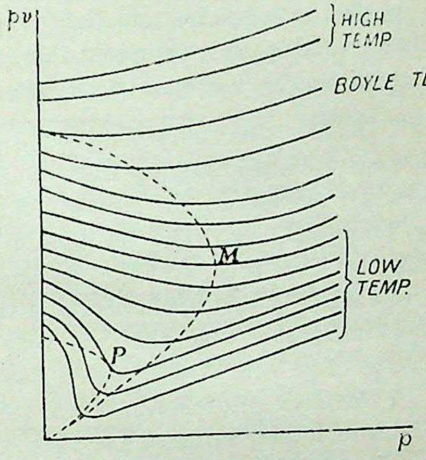


Fig. 162. Curves for carbon dioxide.

The following important points can be gathered from the study of these curves :—

(*i*) the lowest three isothermals (below about 30°C) have a portion of them parallel to the pv-axis, which means that the pressure remains constant while the volume varies, corresponding to the liquefaction of the gas ; P is the critical point.

(*ii*) the curvature of the isothermals diminishes as the temperature rises ; the minima points on the curves gradually recede from the origin and the dotted curve through them is parabolic ; at still higher temperatures no minima points are found and carbon dioxide behaves like hydrogen. The equation of these inclined straight lines is of the form

$$pv = \beta p + \alpha \text{ or } p(v - \beta) = \alpha.$$

(*iii*) In terms of the Boyle temperature, below it pv first decreases with p due to the negative value of B and then increases again ; thus the gas is more compressible in this region than permitted by Boyle's law. Above the Boyle temperature, pv increases with p due to the positive value of B ; thus the gas is less compressible than would be expected from Boyle's law.

These findings suggest that there is *no essential difference between the permanent and liquefiable gases*, all of them behaving similarly towards the perfect gas equation when they are equally remote from their respective critical points, *i.e.*, when they are in, what is known as, *corresponding states*.

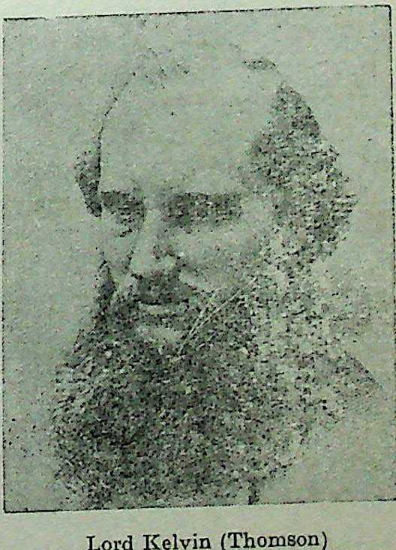
The **fourth and final stage** *in the study of the behaviour of gases* is characterised by the *discovery of inter-molecular attraction* which is the cause of the observed deviations of all actual gases from the perfect gas equation and the *formulation of a new gas equation* which will adequately represent the behaviour of actual gases under all conditions of pressure and temperature.

The fact that below the Boyle temperature, the actual gases are more compressible than a perfect gas suggests the existence of inter-molecular attractions, for they would act in the direction of decreasing compressibility. The increase of pv with p at high pressure indicates, in its turn, that the molecules of the actual gases have a finite size, for it is fundamental that the molecules of matter must repel one another when they are very close. The absence of any decrease of pv with p above the Boyle temperature suggests that either the effect of the finite size of the molecules is greater than that of inter-molecular attraction or that attraction has changed into a repulsion. These factors have to be taken into consideration in formulating an equation suited to actual gases.. Before coming to this point, we shall give an account of the experimental discovery of the existence of inter-molecular attraction by Joule and Kelvin (Thomson) in their important researches, known as the Joule-Kelvin porous plug experiment.

Discovery of inter-molecular attraction—Joule-Thomson Porous Plug experiment. The problem of inter-molecular attraction had attracted the attention of Prof. Joule as early as 1845, in connection with his measurement of mechanical equivalent of heat by finding the heat developed when air was compressed. He rightly thought that the work done on the gas would be equivalent to the heat produced, only if no work was done by the mutual attractions of the molecules as they approached one another when the gas was compressed. He had taken no account of this factor in his experiment and yet found that his values for J agreed so well with those of others. He, therefore, decided to make a more direct investigation in the matter.

When a gas is made to expand without doing external work and without allowing any heat to enter or leave it during the expansion, if the molecules of the gas attract one another, internal work will have to be done in pulling them apart and this can only be achieved at the expense of the heat energy of the gas, which will, therefore, be cooled by the expansion. If the molecules repel one another, the expansion will be accompanied by a rise of temperature, and if there is no inter-molecular attraction there will be no change in temperature.

In order to verify these predictions, Joule took two small steel vessels joined by a tube provided with a tap, exhausted one of them and filled the other with air at a high pressure (about 20 atmospheres). The two vessels were then immersed in a water-bath whose temperature was noted by a sensitive thermometer reading correct to $\frac{1}{200}$th of a degree. Opening the tap, the air was allowed to expand into the exhausted vessel, thus doing no external work. The expansion was so rapid that no heat communication with the surroundings was possible and hence a fall in temperature was expected if inter-molecular attractions existed. He could observe no such fall in temperature, which made him conclude that his experimental set-up was probably too crude, since the evidence in favour of the existence of inter-molecular attraction was very strong from other directions. Later, in 1852, Lord Kelvin (Thomson), in collaboration with Joule, devised a more sensitive technique, known as the "porous plug" experiment and established, beyond doubt, the existence of inter-molecular attractions.



Lord Kelvin (Thomson)

The porous plug experiment. The *principle* of this experiment is to drive a gas by a compressor at a constant pressure through a porous plug and take the temperature of the gas as it enters and leaves the plug. The porous plug consists simply of a porous material, such as cotton, wool, silk, etc., having a number of fine holes or pores and is thus equivalent to a number of narrow orifices in parallel. The plug is surrounded by a non-conducting jacket to prevent any heat from entering or leaving the gas during its passage through the plug. The gas, as it flows through the narrow orifices under a large drop of pressure, gets *throttled* or *wire-drawn*, *i.e.*, the molecules of the gas are drawn apart from one another, so that, if there exist inter-molecular attractions, the gas will have to do internal work, utilizing its own heat energy, as it is thermally isolated, which will be manifested by a drop in its temperature as it issues out of the porous plug. Such a cooling of the gas was actually demonstrated by Joule and Thomson in their porous plug experiment and hence it is called the *Joule-Thomson effect*. It is to be noted that, unlike in the case of Joule's experiment where the gas is made to expand without doing any external work, in the porous plug experiment the gas expands against a constant external pressure and hence it has to do external work or some work is done on it, over and above the internal work against inter-molecular attractions.

The *apparatus* used by Joule and Thomson is shown in Fig. 163. It consists of a porous plug G of silk or cotton wool, kept in position between two perforated brass plates and enclosed in a boxwood tube B to secure thermal isolation. B is surrounded by a brass case D full of cotton wool, which serves as a good thermal insulator and also protects B from coming into contact with water, as the whole apparatus is placed in a water-bath to ensure constant temperature. The boxwood tube is fitted on both sides with copper tubes CC. The lower of these is connected to a compression pump P through a copper spiral S which is also immersed in the water bath to maintain the gas at a constant temperature before it reaches the plug.

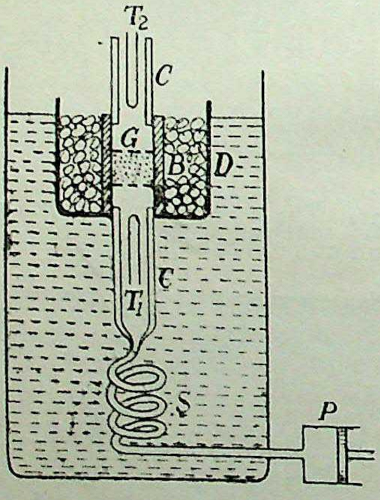


Fig. 163. Porous plug apparatus.

The compressed gas is allowed to suffer *throttle expansion* through the porous plug G which serves to keep down the velocity of flow of gas on emerging and thus prevent the formation of eddy currents. Both these effects are spurious, which will mask the sought for result and hence must be avoided. The temperature of the gas on the two sides of the plug are measured with platinum resistance thermometers T_1 and T_2. The gas is allowed to flow for about an hour in order to obtain the steady state. The experiment is repeated for various differences of pressure on the two sides of the porous plug. The initial pressure of the gas is measured by a manometer (not shown in Fig.) at the entrance into the lower copper tube, while its final pressure is that of the atmosphere. Different gases are investigated over a wide range of temperatures.

Joule and Thomson experimented on air, oxygen, nitrogen and carbon dioxide between 4° and 100°C, the initial and final pressures being 4·5 and 1 atmosphere respectively. Some of the subsequent workers employed a plug of the "radial flow" type (instead of the "axial flow" type of Joule and Thomson), where the gas flowed from the outside of a hollow cylindrical porous plug to inside, thereby securing a better thermal insulation.

The *results* of these experiments may be summarised as follows :—

(*a*) At sufficiently low temperatures all gases show a cooling effect in passing through the porous plug. But at ordinary temperatures most gases show a cooling effect, while hydrogen shows a heating effect.

(*b*) The fall in temperature is proportional to the difference of pressure on the two sides of the porous plug. The greater the difference of pressure the greater the drop in temperature.

(*c*) The fall in temperature per atmosphere difference of pressure decreases as the initial temperature of the gas is raised, becomes zero at a particular temperature, which is different for each gas, and above this temperature there is no more fall but rise in temperature. The temperature, at which the Joule-Thomson effect changes sign, *i.e.*, the cooling effect becomes heating effect, is called the *temperature of inversion*.

(*d*) The magnitude of the effect is shown by the following results obtained. At 0°C, for air 0·275°C cooling per atmosphere, for carbon dioxide 1·39°C cooling per atmosphere and for hydrogen 0·03°C heating per atmosphere.

(*e*) The important conclusion that can be drawn from these results is :—*Any gas below its temperature of inversion will cool on passing through a narrow orifice without resultant work.*

Theory of the experiment. The results stated above can be adequately explained by the following elementary theory.

Let a simple arrangement shown in Fig. 164 represent the parous plug experiment. A certain mass of the gas is flowing through a narrow orifice O from a chamber A to another chamber B, both the chambers being thermally insulated. C and D are two imaginary pistons, the former representing the compresser which drives the gas forward and the latter the pressure of the atmosphere which is being driven back by the gas. The pistons are moved in such a way that the high-pressure in A and the low-pressure in B are kept constant, *i.e.*, a steady difference of pressure is maintained.

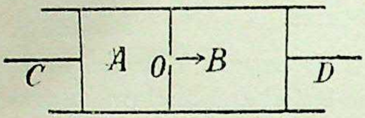


Fig. 164.

Considering unit mass of the gas let p_1, v_1, and T_1 be its pressure, volume and temperature respectively on the high-pressure side and p_2, v_2 and T_2 similar quantities on the low-pressure side. Let U_1 and U_2 be the internal energies of unit mass of the gas in the chambers A and B respectively.

The work done by the piston C on the gas $= p_1 v_1$

The work done by the gas on the piston D $= p_2 v_2$

∴ The net work done by unit mass of the gas in passing through the orifice $= p_2 v_2 - p_1 v_1$.

Since no heat can be gained by the gas from the outside due to thermal insulation, the energy spent by the gas in doing the work must have been derived from a drop of the internal energy of the gas.

Hence $$p_2 v_2 - p_1 v_1 = U_1 - U_2 \qquad \ldots (1)$$

Or $$U_1 + p_1 v_1 = U_2 + p_2 v_2 \qquad \ldots (2)$$

Hence the total heat function $i = U + pv$ remains constant during the throttling process, *i.e.*, the process is *isenthalpic*.

The internal energy of a gas is made up of two parts, *viz.*, *kinetic*, associated with the translatory motion of the molecules which is responsibe for the heat energy and hence for the temperature of the gas, and *potential*, resulting from the force of attraction between the molecules. If k_1 and ρ_1 represent the kinetic and potential energies respectively of the gas in the chamber A and k_2 and ρ_2 similar quantities in the chamber B, then

$$U_1 = k_1 + \rho_1 \quad \text{and} \quad U_2 = k_2 + \rho_2 \qquad \ldots (3)$$

Also $$T_1 \propto k_1 \quad \text{and} \quad T_2 \propto k_2, \text{ so that}$$

$$\left.\begin{array}{ll} \text{if} & T_1 > T_2, \text{ then } k_1 > k_2 \\ \text{and if} & T_1 < T_2, \text{ then } k_1 < k_2 \end{array}\right\} \qquad \ldots (4)$$

We are now in a position to discuss the behaviour of gases at various temperatures.

In the case of a *perfect gas*, since *Boyle's law is obeyed*,

$$p_1v_1 = p_2v_2$$

$$\therefore \qquad U_1 = U_2 \qquad \text{from eqn. (1)}$$

$$\text{Or} \qquad k_1 + \rho_1 = k_2 + \rho_2 \qquad \text{from eqn. (3)}$$

But, as there are no forces of attraction between the molecules of a perfect gas, by assumption,

$$\rho_1 = \rho_2 = 0$$

$$\therefore \qquad k_1 = k_2 \text{ or } T_1 = T_2$$

Hence, on theoretical grounds at least, there is no change of temperature in the process of expansion through the orifice. But, as we know, a perfect gas is an ideal, not found in nature.

Coming to *actual gases*, two cases can be distinguished :—

(*i*) *Below the Boyle temperature,* experiments show that pv decreases with increase of p during the initial stages of compression (*Cf*. Fig. 162). Hence $p_1v_1 < p_2v_2$

or $\quad p_2v_2 - p_1v_1$ is a + ve quantity

$\therefore \quad U_1 - U_2$ is a + ve quantity

or $\quad U_1 > U_2$

i.e., $\quad k_1 + \rho_1 > k_2 + \rho_2$

Since, if there exist inter-molecular attractions, expansion causes increase of potential energy of the molecules, as already indicated, $\quad \rho_2 > \rho_1$

$$\therefore \qquad k_1 > k_2 \text{ and } T_1 > T_2$$

Hence the process of internal work against inter-molecular attractions will result in *cooling*.

Considering the deviation from Boyle's law, since $p_2v_2 > p_1v_1$, the *gas does a little external work* in passing through the orifice and this of itself will produce *cooling* due to the adiabatic expansion, even if there were no inter-molecular attractions. The coolings due to the two processes will add up.

(*ii*) *Above the Boyle temperature,* since pv increases with increase of p (*Cf*. Fig. 162) $p_1v_1 > p_2v_2$

$\therefore \quad p_2v_2 - p_1v_1$ is a −ve quantity

and $\quad U_1 - U_2$ is a −ve quantity

or $\quad U_1 < U_2$

i.e., $\quad k_1 + \rho_1 < k_2 + \rho_2$

If there exist inter-molecular attractions, the potential energy will increase due to expansion and hence the kinetic energy will decrease, *i.e.*, $\rho_2 > \rho_1$ and $k_2 < k_1$. A *cooling effect* will be produced. This, however, does not justify the relation $k_1 + \rho_1 < k_2 + \rho_2$. But considering the deviation from Boyle's law, since $p_2v_2 < p_1v_1$, the *gas has a little external work done on it* in passing through the orifice, which will produce a *heating effect*. As the effects of the processes are opposed, there may be a *net heating effect, null effect or a net cooling effect*, depending on the predominance of one process over the other or on their equal strength.

Thus, we see that the Joule-Thomson effect is made up of two parts, one due to inter-molecular attractions and the other due to the small amount of external work done by or on the gas. *At the temperature of inversion*, which is well above the Boyle temperature, the cooling due to inter-molecular attractions is just balanced by the heating due to the external work done on the gas. *Above the temperature of inversion*, the latter effect outbalances the former, which, however, seems to be decreasing. Expansion in this case will result in decrease of potential energy and $\rho_1 > \rho_2$ and in consequence $k_2 > k_1$, which follows from the relation $k_1 + \rho_1 < k_2 + \rho_2$ and means that $T_2 > T_1$, *i.e.*, heating effect. *Below the temperature of inversion*, the effects due to the two processes are cooling.

The slight heating obtained in the case of hydrogen at ordinary temperature is entirely accounted for by the external work done on the gas, since its temperature of inversion is −80°C. The deviations from Boyle's law of hydrogen at ordinary temperatures are known to be small, and the reason is that they are due solely to the finite size of the molecules.

This discussion leads to the conclusion that the lower the temperature of the gas, Joule-Thomson cooling will be greater for the same difference of pressure. And this is experimentally verified. Air, for instance, shows a cooling of 0·152°C per atmosphere at 93°C, but 0·263°C per atmosphere at 7°C; carbon dioxide has a fall of 0·645°C per atmosphere at 96°C and 1·233°C per atmosphere at 8°C. Hydrogen at ordinary temperatures (30°C) shows a heating of 0·039°C per atmosphere, while a heating of only 0·004°C per atmosphere at −71°C. At its temperature of inversion (−80°C) the heating effect will disappear and below that temperature it will also produce cooling effect like other gases. Hence, the lower the temperature of the gas, the inter-molecular attractions become more effective which render the gas less perfect.

Before proceeding further, let us recapitulate the main results obtained in the investigations made for solving the problem of liquefaction of gases. The essential similarity of all actual gases, permanent or otherwise, is established from the following facts : (*i*) Both the permanent and the liquefiable gases possess inter-molecular attraction, a condition essential to the realisation of the liquid state. (*ii*) The permanent gases show the same kind of deviation from Boyle's law as the liquefiable gases under conditions remote from the point of liquefaction. (*iii*) The liquefiable gases, in their turn, have a critical temperature, above which even they cannot be liquefied. Hence the whole problem reduces to the finding of the critical temperature and the corresponding pressure. This is a comparatively easy matter in the case of gases, which have been liquefied. But how are these critical constants to be found in the case of gases which have not been liquefied ? This question has been solved elegantly by formulating an equation of state which fits actual gases better than the perfect gas equation, taking into account the inter-molecular attraction and the finite size of the molecules. We, therefore, take up the study of the new equation of state holding good in the case of actual gases.

Van der Waals' equation of state for actual gases. Van der Waals was the first, in 1879, to propose a new equation of state for actual gases. He was guided in this attempt by the following line of argument. The kinetic theory of gases, basing itself on the two fundamental assumptions, *viz.*, the molecules were mere point-masses having no dimensions and they did not exert forces of attraction on one another, had fully justified the perfect gas equation (as we have seen in the last chapter). But experiments over a wide range of pressure and temperature showed that actual gases deviated from the perfect gas equation and the general nature of the deviations, being small at low pressure and high temperature, large at high pressure and low temperature, suggested that they were due to mutual attraction between the molecules and the finite size of the molecules.

Van der Waals

The Joule-Thomson effect gave a direct proof of the existence of inter-molecular attractions. Hence in the modification of the perfect gas equation to cover the behaviour of actual gases, the two assumptions of the kinetic theory of gases had to be revised and the new equation must take account of the finite size of the molecules and inter-molecular attraction.

Correction for the finite size of the molecules. Let CDEF represent a closed space of volume v containing the gas, in which the molecules of the gas are assumed to move (Fig. 165). For our present purpose, the molecules are considered as hard elastic spheres with a finite radius. Suppose a molecule, moving parallel to CD, travels between the walls CF and DE to and fro. If CD $= l$, the distance travelled in one complete trip from CF to DE and back to CF is not $2l$, but $2l - 2d$, where d is the diameter of the molecule. If we consider the motion of all the molecules in this way, we find that the effective volume in which the molecules move is less than the total volume v of the enclosure. It is also clear that at very high pressures the total volume of all the molecules is not a negligible fraction of the volume of the gas and further even at the highest possible pressure the volume occupied by the substance cannot be less than the volume occupied by the molecules when they are most closely packed. It follows therefore that when the pressure is increased, there is a decrease not in the whole volume v, as used in the perfect gas equation, but in a less volume $(v - b)$, where b is a constant related to the total volume of the molecules.

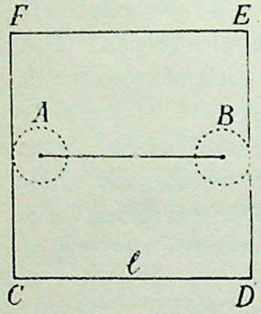


Fig. 165.

Correction for the inter-molecular attraction. The inter-molecular forces in a gas are probably of the same nature as those which give rise to the phenomenon of surface tension in liquids, and are due to some sort of magnetic and electric influence. The molecules attract one another with a force which varies inversely as some power of the distance between them, so that the attraction is appreciable only for small distances and is negligible for larger ones and hence each molecule can be thought of as being surrounded by a sphere of influence, inside which alone other molecules can exert any force on it.

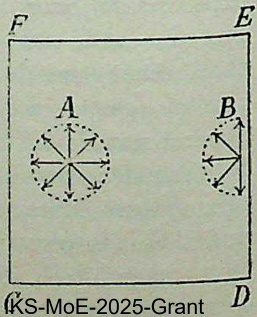


Fig. 166.

Considering a molecule at a point A (Fig. 166), in the interior of the mass of the gas, it is unaffected by inter-molecular attractions, since it is being attracted equally in all directions and the forces cancel one another out. But when it finds itself at a point B near a wall of the enclosure, it will experience a pull towards the interior due to the unbalanced molecular forces. This pull directed towards the interior and normal to the wall increases from a minimum at a distance equal to the radius of the sphere of influence to a maximum just when the molecule is about to impinge on the wall. Hence the molecule will strike the wall with a velocity less than that with which it would have struck in the absence of inter-molecular attraction. This is true of every molecule striking the walls of the enclosure. The velocity and hence the momentum with which the molecules strike the walls is, therefore, reduced due to inter-molecular attractions. When the momentum is less, the pressure exerted by the gas is also less.

The magnitude of this decrease in pressure may be estimated as follows :—The decrease in pressure is evidently proportional to the number of attracting molecules per unit volume and to the number of attracted molecules that strike unit area of the wall per unit time. Both these factors are proportional to the number of molecules in unit volume of the gas, or to the density of the gas.

$$\begin{aligned}\text{Hence decrease of pressure} &\propto (\text{density of the gas})^2\\ &\propto 1/v^2\\ &= a/v^2\end{aligned}$$

where a is a constant of proportionality.

Therefore if the effect of inter-molecular attractions is taken into account, the corrected expression for the pressure must be equal to the sum of the observed pressure p and the decrease in pressure (a/v^2) caused by such attractions.

Hence, introducing the two corrections due to the finite size of the molecules and the inter-molecular attractions, the perfect gas equation is modified as

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{RT} \qquad \dots (1)$$

which is Van der Waals' equation.

Van der Waals estimated the values of the constants a and b appearing in his equation as follows :—From the change of pressure with temperature of the gas kept at constant volume a can be estimated ; from the change in pv with change of p at constant temperature b can be evaluated. The values of a and b are usually expressed in atmospheres and in c.c. respectively. The values of a and b are however ordinarily evaluated from the critical constants. We shall presently see that the critical constants can be expressed in terms of a, b and R. Hence if the former are determined experimentally, the latter can be found. It must be said, however, that this method is not very accurate, since the gas does not obey Van der Waals' equation accurately near the critical point. But this is not of great consequence, since a and b themselves depend upon temperature and volume. It is evident that the values of a and b will be different for different gases.

Checking the validity of Van der Waals' equation by comparison with experimental facts. (*i*) *Andrews' isothermals for carbon dioxide.* Van der Waals' equation can be put in the form :

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad \dots (2)$$

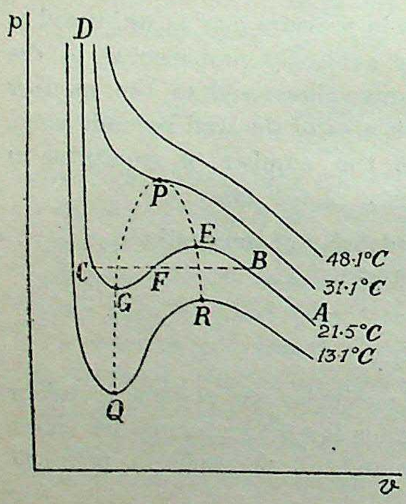


Fig. 167. Theoretical curves for CO_2 using Van der Waals' equation.

Substituting the known values of a and b for carbon dioxide and of R, graphs relating p and v at different temperatures can be plotted. The curves obtained are of the form shown in Fig. 167. The curves are bound to be complex. From the above relation, we see that for very large values of v, p is small and in the limit $p = 0$ when $v = \infty$. When v is very small approaching b, p tends to infinity. Hence the curves should be concave upwards. These theoretical curves resemble in a striking manner the experimental curves obtained by Andrews (*Cf.* Fig. 155), except for the horizontal portions at lower temperatures, where smoother variations occur with maxima and minima points. Even this discrepancy has been explained by James Thomson as representing unstable conditions of supersaturated vapour and superheated liquid (*Cf.* p. 390).

Critical constants. The maxima and minima points exhibited by the lower isothermals can be obtained by putting $\frac{dp}{dv} = 0$. Hence differentiating relation (2) and equating it to zero,

$$\frac{dp}{dv} = - \frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

or

$$RT = \frac{2a\,(v-b)^2}{v^3}. \qquad \ldots (3)$$

This, being a cubic equation in v, for every isothermal there are three real or one real and two imaginary points of maxima or minima. The curves below P in Fig. 167 have one maxima and one minima point, while those above it have none at all ; the other point of minima lies in the region $v < b$ and hence has no physical significance.

Taking relation (1) and substituting for RT from relation (3), we have

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = \frac{2a\,(v-b)^2}{v^3}$$

or

$$\left(p + \frac{a}{v^2}\right) = \frac{2a\,(v-b)}{v^3}$$

$$\therefore \qquad p = \frac{2a\,(v-b)}{v^3} - \frac{a}{v^2} \qquad \ldots (4)$$

This relation (4) gives the dotted curve RPQ passing through the maxima and minima points. *The maximum point P on this curve is evidently the critical point of the gas.* For, below P every isothermal has got maxima and minima points, while above P no isothermal has any maxima or minima, which means that there is no abrupt change from the gaseous to the liquid state in going along any isothermal above P, *i.e.*, to say that the properties of the liquid and gaseous states have now merged together, or, in other words, the gas is above its critical temperature. Again, for liquefaction there must be two points on the curve having equal pressures as in the isothermals below P. The highest isothermal for which this condition is satisfied is the one passing through the point P, since at P the maxima and minima points coalesce into one. This isothermal through P is evidently the *critical isothermal.*

The volume, pressure and temperature represented by the point P are, therefore, the critical constants of the gas. Expressions for them can be readily deduced, using the fact that P is the maximum point of inflexion in the dotted curve. Differentiating, therefore, relation (4) which represents this curve and equating it to zero, we get

$$\frac{2a}{v^3} - \frac{6a\,(v - b)}{v^4} + \frac{2a}{v^3} = 0$$

$$\therefore \qquad \frac{4a}{v^3} = \frac{6a\,(v - b)}{v^4}$$

The v in this expression evidently represents the *critical volume* v_c.

$$\therefore \qquad 4a = \frac{6a\,(v_c - b)}{v_c}$$

or

$$v_c = 3b \qquad \dots (5)$$

Substituting this value of v_c in relation (4), we get an expression for the *critical pressure* :—

$$p_c = \frac{2a\,(3b - b)}{27\,b^3} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{a}{9b^2}$$

$$= \frac{a}{27b^2} \qquad \dots (6)$$

Substituting the value of v_c in relation (3), an expression for the *critical temperature is obtained* :—

$$\mathrm{RT}_c = \frac{2a\,(3b - b)^2}{27b^2} = \frac{8a}{27b}$$

$$\therefore \qquad \mathrm{T}_c = \frac{8a}{27b\mathrm{R}} \qquad \dots (7)$$

It may be noted that the critical constants are deduced from relation (2) by taking

$$\frac{dp}{dv} = 0 \text{ and } \frac{d^2p}{dv^2} = 0 \text{ at the critical point.}$$

Hence, if the Van der Waals' constants a, b and R are known, the critical constants can be calculated. Thus, for example, Van der Waals obtained in the case of carbon dioxide the values 0·00874 atmosphere and 0·0023 c.c. for a and b respectively.

Assuming $p = 1$ atmosphere, $v = 1$ c.c. and T = 0°C or 273°K, the corresponding value of R can be obtained by substituting the values of p, v, a, b and T in the Van der Waals' equation :—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

$$\left(1 + \frac{\cdot 00874}{1^2}\right)(1 - \cdot 0023) = \mathrm{R} \times 273$$

$$\therefore \qquad R = \frac{1{\cdot}00874 \times {\cdot}9977}{273}$$

$$\text{Hence } T_c = \frac{8a}{27Rb} = \frac{8 \times {\cdot}00874 \times 273}{27 \times 1{\cdot}00874 \times {\cdot}9977 \times {\cdot}0023}$$

$$= 305{\cdot}5°\text{K} = 32{\cdot}5°\text{C}$$

This value agrees approximately with the experimental value of 30·9°C obtained by Andrews for carbon dioxide. In the case of other gases also, the agreement between the theoretical and experimental values is only approximate, except for the halogen derivatives of benzene, where it is quite good. It may be noted that for our immediate purpose of liquefying gases, it is not necessary to have a complete agreement between theory and experiment, since it is enough to have an approximate idea of the critical temperature in order to realise how far a gas has to be cooled roughly to liquefy it by the application of a suitable pressure. This is certainly furnished by the Van der Waals' equation, which is no small merit in its favour.

(*ii*) *Amagat's curves.* Taking Amagat's experimental compressibility curves, qualitatively represented in Fig. 168, at ordinary temperatures, pv diminishes with increase of p, reaches a minimum value and then increases in the case of CO_2 and N_2, while H_2 does not show any such minimum value at all for the same temperature. The Van der Waals' equation provides an explanation for this peculiar behaviour of gases :

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$$

$$pv + a/v - pb = RT,$$

neglecting $\frac{ab}{v_2}$.

$$\therefore \; pv = RT + \left(bp - \frac{a}{v}\right) \quad \ldots (8)$$

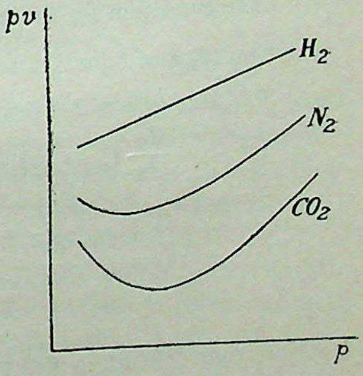


Fig. 168.

From this relation (8), we see that pv will be greater or less than RT = product of pressure and volume of a perfect gas, according as $\left(bp - \frac{a}{v}\right)$ is +ve or −ve. Now for hydrogen, $\frac{a}{v}$ is almost zero, so that if pv and p are plotted for different temperatures, the curves will all be straight lines, but inclined to the p-axis, as experimentally found by Amagat. If $bp < \frac{a}{v}$, then pv will go on diminishing as p increases, until p is large enough to make $bp = a/v$. Just at that point $pv = \mathrm{RT}$, the curve will be horizontal ; beyond this, pv will increase with pressure. For N_2 and especially CO_2 the experimental curves are according to this theoretical prediction. Further, according to the Van der Waals' equation, even hydrogen will show a minimum at low temperatures. The temperature at which the minimum occurs can be found thus :—

Let x and y be the co-ordinates of the minimum point in the pv vs. p curve, *i.e.*, $y = pv$ and $x = p$ or $\frac{1}{v}$.

Taking the Van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

$$\left(pv + \frac{a}{v}\right)\left(1 - \frac{b}{v}\right) = \mathrm{RT}$$

$$(y + ax)(1 - bx) = \mathrm{RT}$$

$$\therefore \quad y(1 - bx) + ax(1 - bx) = \mathrm{RT} \qquad \ldots (9)$$

The condition for the minimum point is $\frac{dy}{dx} = 0$. Hence differentiating (9) and equating to zero,

$$dy\,(1 - bx) - yb.dx + a.dx - axb.dx - bxa.dx = 0$$

$$\text{Or} \qquad \frac{dy}{dx}(1 - bx) + a(1 - bx) - b(y + ax) = 0$$

$$\therefore \qquad \frac{dy}{dx} = \frac{b(y + ax) - a(1 - bx)}{(1 - bx)}$$

$$= b\left(\frac{y + ax}{1 - bx}\right) - a$$

But from (9), $(y + ax) = \frac{\mathrm{RT}}{1 - bx}$

$$\therefore \qquad \frac{dy}{dx} = \frac{b\mathrm{RT}}{(1 - bx)^2} - a$$

$$\text{But} \qquad \frac{dy}{dx} = 0$$

$$\text{Hence} \qquad \frac{b\mathrm{RT}}{a} = (1 - bx)^2$$

$$\text{or} \qquad 1 - bx = \sqrt{b\mathrm{RT}/a}$$

$$\therefore \qquad bx = 1 - \sqrt{b\mathrm{RT}/a}$$

If $\sqrt{bRT/a} < 1$, x is positive and the minimum point will lie to the right of the Y-axis ; if $\sqrt{bRT/a} > 1$, x is negative and the minimum point will lie to the left of the Y-axis ; this is the case with hydrogen, since for it a is very small, so that bRT becomes great even at ordinary temperatures ; that is why the minimum point for hydrogen is not found on the right side of the pv-axis. If $\sqrt{bRT/a} = 1$, $x = 0$, and the minimum point will lie on the Y-axis itself. Since, b, R and a are constants, only by controlling T, the minimum point can be made to be either on the +ve, or −ve side of the Y-axis, or on the Y-axis itself. For the minimum point to lie on the pv-axis itself, the condition is that $T = \frac{a}{bR}$. The temperature at which pv is a minimum may also be regarded as that temperature at which the gas just begins to behave like hydrogen, or if the minimum point is on the Y-axis itself, the gas just begins to behave like hydrogen from the Y-axis. Calling this transition temperature T_B,

$$T_B = \frac{a}{bR}.$$

Since $$T_c = \frac{8a}{27Rb}, \quad T_B = \frac{27}{8}\,T_c$$

or $$T_B = 3{\cdot}375\ T_c$$

Hence, according to theory, every gas, even CO_2 included, will behave like hydrogen on the −ve side of pv-axis at temperature equal to 3·375 times its critical temperature. Although this prediction is verified to a certain extent by experiment, T_B, which is the *Boyle temperature*, is found to be only 2·98 or 3 times T_c.

(*iii*) *Corresponding states.* We have already mentioned that substances that are equally remote from their respective critical points behave in a similar manner and hence said to be in corresponding states (*Cf*. p. 397). This also receives an explanation on the Van der Waals's equation.

Taking $\left(p + \frac{a}{v^2}\right)(v - b) = RT$, let $p = \pi\, p_c$, $v = \varphi\, v_c$ and $T = \eta\, T_c$,
where the actual pressure, volume and temperature of a gas are expressed as multiples of the respective critical values. If two gases have the same values for π, φ and η, they are said to be in corresponding states. It follows also that if two gases have the same value for π and φ, they must have the same value for η.

Substituting these values of p, v, T in the above equation

$$\left(\pi p_c + \frac{a}{\varphi^2 v_c^2}\right)(\varphi\, v_c - b) = \mathrm{R}\eta \mathrm{T}_c$$

Replacing p_c, v_c and T_c by their respective values,

$$\left(\pi \frac{a}{27b^2} + \frac{a}{\varphi^2 \,.\, 9b^2}\right)(\varphi . 3b - b) = \mathrm{R}\eta \frac{8a}{27\mathrm{R}b}$$

Simplifying,

$$\left(\frac{\pi}{27} + \frac{1}{9\varphi^2}\right)(3\varphi - 1) = \frac{8\eta}{27}$$

This relation is independent of the constants a, b, R which are different for different gases, and will, therefore, represent the behaviour of all gases equally well, provided they have the same values for π, φ and η. It is known as the *corresponding state equation* or *reduced Van der Waals' equation* or even simply as the *reduced isothermal.* It is to be noted that this explanation has only a qualitative significance, in that it leads to the *law of corresponding states*, *viz.*, if two gases have the same reduced pressure and volume, they have also the same reduced temperature, since if they have the same values for π and φ, they must have also the same value for η.

(*iv*) *Joule-Thomson effect.* When a gas is allowed to expand through a porous plug from a pressure p_1 and volume v_1 to a pressure p_2 and volume v_2, its temperature changes from T_1 to T_2 due to Joule-Thomson effect. During the expansion the gas does external work as well as internal.

The external work done by the gas $= p_2v_2 - p_1v_1$

The internal work is done in overcoming the forces of intermolecular attraction. In the Van der Waals' equation it is assumed that the pressure of gas decreases by $\frac{a}{v^2}$ due to inter-molecular attraction.

Hence, when the gas expands from a volume v_1 to v_2, the internal work done by it

$$= \int_{v_1}^{v_2} \frac{a}{v^2}\, dv$$

$$= \frac{a}{v_1} - \frac{a}{v_2}$$

$\therefore$ Total work done by the gas

$$\mathrm{W} = p_2v_2 - p_1v_1 + \frac{a}{v_1} - \frac{a}{v_2} \qquad (1)$$

Taking the Van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{RT}$$

$$pv + a/v - pb = \mathrm{RT}, \text{ neglecting } \frac{ab}{v^2}.$$

$$\therefore \qquad pv = \mathrm{RT} + \left(bp - \frac{a}{v}\right) \qquad \ldots (2)$$

Substituting this value of pv, in equation (1) with the appropriate suffixes

$$\mathrm{W} = \mathrm{RT}_2 + bp_2 - \frac{a}{v_2} - \mathrm{RT}_1 - bp_1 + \frac{a}{v_1} + \frac{a}{v_1} - \frac{a}{v_2}$$

$$= \mathrm{R}(\mathrm{T}_2 - \mathrm{T}_1) - \frac{2a}{v_2} + \frac{2a}{v_1} - b(p_1 - p_2) \qquad \ldots (3)$$

Since a and b are very small, we may take approximately $pv = \mathrm{RT}$ or $v = \frac{\mathrm{RT}}{p}$.

Substituting this value of v in equation (3) with the appropriate suffixes

$$\mathrm{W} = \mathrm{R}(\mathrm{T}_2 - \mathrm{T}_1) - \frac{2ap_2}{\mathrm{RT}_2} + \frac{2ap_1}{\mathrm{RT}_1} - b(p_1 - p_2)$$

Since T_1 and T_2 differ very little from each other, we may write $d\mathrm{T} = \mathrm{T}_1 - \mathrm{T}_2$ and $\mathrm{T} = \mathrm{T}_1 = \mathrm{T}_2$.

$$\therefore \mathrm{W} = -\mathrm{R}d\mathrm{T} + \frac{2a}{\mathrm{RT}}(p_1 - p_2) - b(p_1 - p_2)$$

$$= (p_1 - p_2)\left(\frac{2a}{\mathrm{RT}} - b\right) - \mathrm{R}d\mathrm{T} \qquad \ldots (4)$$

As the gas is thermally insulated, the energy required for doing the above work is derived from the kinetic energy of the molecules. This results in the decrease of the kinetic energy and the consequent fall of temperature by $d\mathrm{T}$. If C_v is the specific heat of the gas at constant volume, the quantity of heat absorbed from the gas itself to do the work W is $\mathrm{C}_v.d\mathrm{T}$. Hence,

$$\mathrm{C}_v.d\mathrm{T} = (p_1 - p_2)\left(\frac{2a}{\mathrm{RT}} - b\right) - \mathrm{R}d\mathrm{T}$$

$$\text{or} \qquad d\mathrm{T}\,(\mathrm{C}_v + \mathrm{R}) = (p_1 - p_2)\left(\frac{2a}{\mathrm{RT}} - b\right)$$

$$\text{Since} \qquad \mathrm{C}_p - \mathrm{C}_v = \mathrm{R},$$

$$\mathrm{C}_p \,.\, d\mathrm{T} = (p_1 - p_2)\left(\frac{2a}{\mathrm{RT}} - b\right)$$

$$\therefore \qquad dT = \frac{p_1 - p_2}{C_p}\left(\frac{2a}{RT} - b\right) \qquad \dots (5)$$

In this relation (5),

if $\frac{2a}{RT} > b$, then dT is positive, which means a cooling effect, since dT represents a lowering of temperature ;

if $\frac{2a}{RT} < b$, then dT is negative and hence there will be a heating effect ;

if $\frac{2a}{RT} = b$, $dT = 0$, and no change of temperature.

The *temperature of inversion* T_i, at which the Joule-Thomson effect is zero, is given by the relation $\frac{2a}{RT} = b$ or $T_i = \frac{2a}{Rb}$.

Since the Boyle temperature $T_B = \frac{a}{Rb}$, $T_i = 2T_B$, *i.e.*, the temperature of inversion is twice the Boyle temperature. Since $T_B = \frac{27}{8} T_c$, $T_i = \frac{27}{4} T_c = 6{\cdot}75\ T_c$, In the following table, the values of T_i calculated from this relation are given for a few gases which have been used in the porous plug experiment.

gas	T_c	T_i
Carbon dioxide	31°C	1779°C
Air	−140°C	624·8°C
Oxygen	−118°C	773·3°C
Nitrogen	− 147°C	577·5°C
Hydrogen	−239·9°C	−49·6°C
Helium	−268°C	−239·3°C

The values of T_i thus calculated from theory are found to agree only approximately with experimental observations. Thus, for instance, for hydrogen at 100 atmospheres pressure $T_i = -80°C$ and not $-49{\cdot}6°C$. The discrepancy may be due to the high pressure, since T_i depends very much on the initial pressure of the gas.

If the temperature at which the experiment is conducted is above T_i, $2a/RT < b$ and there will a heating effect. Hence at ordinary temperatures, hydrogen and helium will produce a heating effect, whereas the other gases such as oxygen, nitrogen, air, carbon dioxide, etc. will produce a cooling effect, since their temperatures of inversion are very high. With hydrogen, a cooling effect is observed if it is cooled below —80°C and then passed through the porous plug.

Limitations of Van der Waals' equation. We have seen above that in spite of general agreement, deductions from the Van der Waals' equation show considerable deviation from experimental results. We shall now mention a few more facts which bring out its defective nature with still greater force :—

(*i*) The *values of a and b* obtained by different methods do not agree ; nay more, the values obtained even by a single method vary considerably at different temperatures. This indicates a fundamental drawback in the equation which cannot be easily remedied by suitable corrections.

(*ii*) *Critical coefficient.* The expression RT_c/p_cv_c is known as the 'critical coefficient'. For a perfect gas, it is equal to unity. In the case of actual gases obeying the Van der Waals' equation, it can be readily estimated from the values of T_c, p_c and v_c.

$$\frac{RT_c}{p_cv_c} = R \times \frac{8a}{27Rb} \times \frac{27b^2}{a} \times \frac{1}{3b}$$
$$= \frac{8}{3} = 2{\cdot}66.$$

The critical coefficient must evidently have the same value for all the gases, if Van der Waals' equation is correct. Actually, however, it is found to vary from gas to gas, the values ranging from 3·28 for hydrogen to 4·99 for acetic acid ; it thus seems to depend upon the molecular structure of the gas. Further, none of the gases examined has a value less than 3, which is decidedly greater than the theoretical value of 2·66.

(*iii*) *Critical volume.* While, according to theory $v_c = 3b$ for all gases, experiments show that the volume of v_c varies from $1{\cdot}4b$ for argon to $2{\cdot}8b$ for hydrogen. Hence the Van der Waals' equation is not obeyed exactly by any gas near its critical point.

We may sum up the situation by saying that, although the Van der Waals' equation succeeds in explaining the deviations from the perfect gas common to all actual gases, it breaks down when applied to the differences between the various gases. Hence other equations have been suggested by Dieterici, Clausius and others to account for these differences, but they appear to belong to the category of '*ad hoc* hypotheses' introduced to arrive at the right result, without being much more successful than the simpler Van der Waals' equation. At any rate, we shall rest satisfied with this equation, as it fully serves the present purpose of solving the problem of liquefaction of the so-called permanent gases by allowing their critical temperatures to be estimated to a first approximation.

Methods employed in the liquefaction of gases. The various methods employed to liquefy gases may be classified under the following three heads :

1. *Cascade process*, which utilises a series of liquids with successively lower boiling points to reach the low temperature in stages.

2. *Regenerative Joule-Thomson process* based on the Joule-Thomson effect and regenerative cooling.

3. *Adiabatic expansion process* based on the cooling produced when a gas expands adiabatically doing external work.

The **cascade process** works on the same general *principle* as was employed in Faraday's experiments, *viz.*, to cool the gas sufficiently and apply simultaneously a large pressure. But the cooling is done in stages using different liquids of successively lower boiling points. On account of this fact, the method is called *cascade* or *series refrigeration*.

Pictet, in 1878, was the first to liquefy oxygen by this method. He employed compression machines containing sulphur dioxide and carbon dioxide to reach the critical temperature of oxygen and obtained intermittent jets of liquid oxygen by allowing compressed oxygen in the final stage to expand adiabatically. Wroblewski and Olszewski obtained sufficient quantities of liquid oxygen, nitrogen and carbon monoxide by this method and studied their properties. Olszewski used a third stage with ethylene after the carbon dioxide and could thereby cool these gases below their critical temperatures. Kamerlingh Onnes employed methyl chloride and ethylene in this process to liquefy oxygen continuously, which has been developed into a commercial method.

The apparatus used by Kamerlingh Onnes is shown in Fig. 169. It consists of three units, each of which comprises of a compression pump and condenser. In the first unit methyl chloride is liquefied. Since the critical temperature of methyl chloride is 143°C, it can be liquefied at the room temperature with a pressure of a few atmospheres. Compressed methyl chloride gas from pump P_1 is passed through the spiral tube (shown straight in the figure) inside the condenser A, while cold water is circulated through the outer jacket of A. Liquid methyl chloride thus obtained is made to circulate the jacket of the condenser B of the second unit, which is connected to the suction side of P_1; this enables the liquid methyl chloride, which normally boils at $-24°C$, to evaporate under reduced pressure and produce a fall of temperature to about $-90°C$ in B. Compressed ethylene from pump P_2 is passed through the spiral tube inside B. Since it has a critical temperature of 10°C, it is readily liquefied in B maintained at about $-90°C$ by the continuous circulation of liquid methyl chloride through it. Liquid ethylene formed in B is made to flow round the jacket of the condenser C of the third unit and at the same time allowed to evaporate under reduced pressure by connecting the jacket of C to the suction side of P_2. The temperature of C thereby falls to about $-160°C$, although the normal boiling point of ethylene is $-104°C$. Compressed oxygen from the pump P_3 passes through the spiral tube inside C where it is easily liquefied since its critical temperature is only $-118°C$. Liquid oxygen is collected in a Dewar flask D.

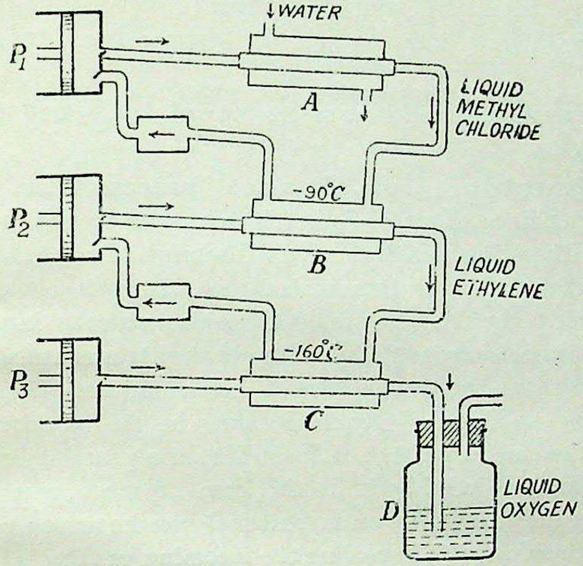


Fig. 169. Cascade process.

Liquid oxygen whose normal boiling point is $-183°C$, in its turn, can be boiled under reduced pressure and the lowest temperature thereby obtained is $-218°C$. Using a fourth unit and passing the liquid oxygen through the jacket of the condenser of that unit, *air can be liquefied* by allowing it to flow at high pressure through the tube inside the condenser, since its critical temperature is only $-140°C$. As the liquid air boils off it becomes richer in oxygen since nitrogen boils away more easily. But neon ($T_c = -229°C$), hydrogen ($T_c = -240°C$) and helium ($T_c = -268°C$) cannot be liquefied by this method, since no liquefied gas is found which will develop such low temperatures by evaporation under reduced pressure.

The method is a little cumbersome and hence not much used now-a-days.

Regenerative Joule-Thomson process. The *principles* involved in this method are Joule-Thomson effect and regenerative cooling. The utilisation of the Joule-Thomson effect has two great advantages over the previous method, *viz.*, (*i*) it is enough to cool the gas below the temperature of inversion, whereas in the cascade process it is necessary to go below the critical temperature, which is much lower than the temperature of inversion, and (*ii*) much less preliminary cooling is required than in the previous process. Further, the chief drawback of Joule Thomson process, *viz.*, the very small cooling produced by it in the case of most gases has been effectively surmounted by an ingenious device known as regenerative cooling, which consists in cooling the incoming gas by a portion of the gas which has already been cooled by Joule-Thomson expansion. In this way the cooling effect is made cumulative and by maintaining a continuous cycle of operation, the initial temperature can be progressively and rapidly lowered, due also to the fact that the lower the temperature the greater is the Joule-Thomson cooling. The principle of regeneration applied to heating was discovered by W. Siemens in 1857, but its application to cooling was made later by Linde, Hampson and others.

Linde, in 1895, was the first to use this process for liquefying air. Hampson, almost at the same time, built independently an air liquefying machine based on the same principles but differing from Linde's apparatus in details of construction. Dewar, in 1898, applied the method to liquefy hydrogen and Kamerlingh Onnes, in 1908, to produce liquid helium. We shall here describe Linde's apparatus for liquefying air, Dewar's work on the liquefaction of hydrogen and Onnes' researches on the liquefaction of helium.

Linde's air liquefier. Linde's apparatus shown in Fig. 170 consists of a two-stage compressor P_1 and P_2. Air compressed to a pressure of about 20 atmospheres by P_1 and cooled by passing through a cold-water bath is first freed from carbon dioxide and water vapour by allowing it to flow through caustic potash, calcium chloride and phosphorus pentoxide tubes (the last two not shown in

Fig.). If this is not done, carbon dioxide and water vapour will solidify before the air is liquefied and block the circulation system.

The air then enters the second compressor P_2 where it is compressed to a pressure of about 200 atmospheres. The compressed air next passes through a cooling spiral immersed in a freezing mixture F, where its temperature is lowered to about $-20°C$. The air thus cooled at high pressure enters the liquefying section proper and passes down through the tube A to the nozzle N_1 where it suffers a drop in pressure, the magnitude of which can be controlled by a valve (not shown in Fig.). It issues from the nozzle at about 20 atmospheres and hence has suffered a considerable throttle expansion. This causes the temperature to fall to about $-70°C$. This cooled air is then made to pass through a wider tube B enclosing A and return to the compressor P_2 where it is again compressed to a pressure of 200 atmospheres. On its way to P_2 it cools the next lot of air passing through A, which, therefore, reaches and issues from N_1 at a still lower temperature. As the circulation continues, after the completion of a few cycles, the air is cooled to a sufficiently low temperature.

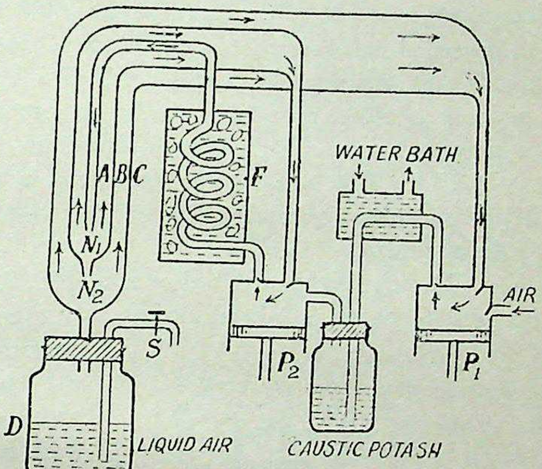


Fig. 170. Linde's air liquefier.

At this stage, the second nozzle N_2 is opened and the already much cooled air is allowed to expand to one atmosphere when it is easily liquefied. The liquid air is collected in a Dewar flask D from which it can be removed by the syphon S. The unliquefied air is led back through the tube C surrounding B to the compressor P_1, for the process to be repeated cyclically. The whole of the liquefying section proper of the apparatus is packed with cotton wool to secure the thermal insulation required in the Joule-Thomson process.

The apparatus built by Linde was worked by a 3 H.P. motor and supplied about one litre of liquid air per hour. Improvements made by Hampson, Dewar and others have rendered it possible for an air-liquefier of this type to produce liquid air within 15 minutes without any preliminary cooling.

Liquefaction of hydrogen. Dewar was the first to succeed in liquefying hydrogen by the Joule-Thomson process. The cascade process fails to liquefy hydrogen on account of its very low critical temperature (−240°C). To utilise the Joule-Thomson process, it has to be cooled first below its temperature of inversion (−80°C), since above that temperature it will produce a heating effect. Furthermore, to obtain appreciable cooling in practice, it has been found necessary to pre-cool hydrogen down to its Boyle temperature (−177°C). This pre-cooling is achieved by passing the gas through liquid air (whose normal boiling point is −190°C) evaporating under reduced pressure.

Dewar's apparatus is shown in Fig. 171. Hydrogen is compressed to about 150 atmospheres and then passed through coils immersed in a cold water bath to remove the heat of compression. It is next freed from carbon dioxide and moisture by passing it through tubes of caustic potash, calcium chloride, etc. These preparatory parts are not shown in Fig. Dry, pure hydrogen thus obtained enters the liquefier and traverses the regenerative coil R in the chamber G which is cooled by the outgoing cold hydrogen gas which has already suffered throttle expansion, and in the final study state becomes cooled to about −170°C. The cooled gass passes through a refrigerating coil A immersed in liquid air contained in a chamber E, and then through another refrigerating coil immersed in liquid air contained in a second chamber F and boiling at a pressure of 10 cms. This is done by allowing liquid air from E to trickle into F and by exhausting F to a pressure of 10 cms.

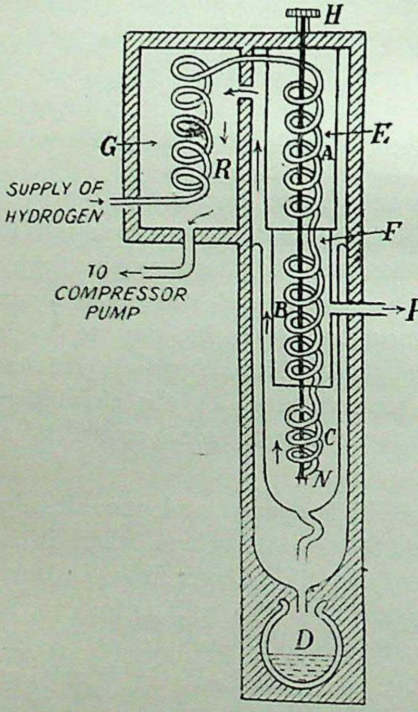
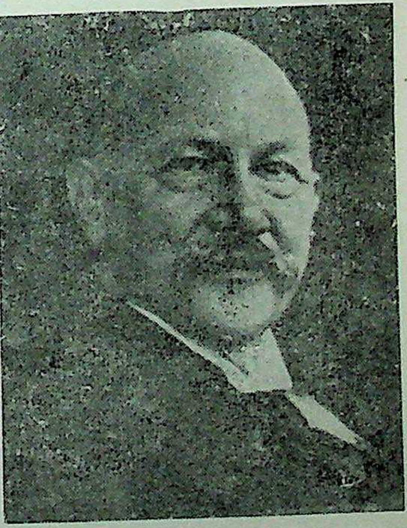


Fig. 171. Dewar's hydrogen liquefier.

through a pump connected at P. The temperature of the gas thus falls to about $-200°C$. After this pre-cooling, the gas passes through the coil C and suffers throttle expansion at the nozzle valve N which is operated from outside the apparatus by the handle H. The gas, thus cooled further, passes up round the chambers F and E, thereby cooling the coils C, B and A, to the chamber G and then to the compressor. After a few cycles, the temperature of the gas reaching N falls to $-250°C$ and the gas under these conditions suffering the Joule-Thomson expansion is liquefied and collected in the Dewar flask D. Liquid hydrogen is transparent and colourless.

Solidification of hydrogen. Dewar, a year later, was able to solidify hydrogen as follows: The liquid hydrogen, whose normal boiling point is $-253°C$, was introduced into a double-walled thermos-tube, and the latter was kept immersed in a bath of liquid hydrogen. The pressure inside the thermos-tube was then reduced to 10 mm., so that the liquid in it could evaporate under reduced pressure, and thereby cooled further. But although a temperature below the freezing point of hydrogen was reached, no solidification occurred due to supercooling. On allowing a trace of air to leak into the apparatus, the liquid hydrogen in the tube solidified into a white solid at a temperature of $-259°C$.

Liquefaction of helium. Helium, the last remaining gas, could not be liquefied for a long time. The attempts made by Dewar and Olszewski by the adiabatic expansion method proved unsuccessful. At last, in 1908, Kamerlingh Onnes, after a tenacious and systematic study of the problem for well over ten years, succeeded to liquefy helium by the Joule-Thomson process. He first cleared the ground by determining the various constants that were implicated in the experiment. Such were the critical temperature $T_c = -268°C = 5°K$, the critical pressure $p_c = 2{\cdot}3$ atmospheres, the normal boiling point $= -268{\cdot}8°C = 4{\cdot}2°K$, the inversion temperature $= -238°C = 35°K$ and the Boyle temperature $= -256°C = 17°K$. He then



K. Onnes

concluded that if helium were to be liquefied by the Joule-Thomson expansion it had to be pre-cooled to 17°K. This temperature he succeeded to obtain by passing pure compressed helium through liquid hydrogen boiling at reduced pressure. The helium gas thus cooled to a temperature of $-258°C = 15°K$ was subjected to throttle expansion when liquid helium was produced. The helium liquefier plant is bound to be complicated due to the use of air and hydrogen liquefiers for pre-cooling purposes. Today there are a number of helium liquefiers in several research laboratories.

It may be noted that helium was later liquefied by Kapitza, Simon and Collins by other methods, such as the adiabatic expansion and desorption methods.

Solidification of helium. Onnes, after liquefying helium, turned his attention to the solidification of liquid helium by evaporating it under reduced pressure. He did not succeed, although he reached a temperature of 1°K. But Keesom, in 1926, was able to produce solid helium, by subjecting the gas to a very high pressure of 130 atmospheres, cooling it in liquid helium and then allowing it to expand. That helium really solidified in this way was established in two ways: (*i*) The circulating system for the liquid helium got blocked by the formation of solid helium ; (*ii*) a magnetically operated metal stirrer in the liquid got stuck eventually indicating thereby the freezing of the liquid ; if the pressure was reduced by a few atmospheres, the tube containing the liquid became clear and the stirrer began to move again. Later experiments showed that helium at 4·2°K solidified under 140 atmos., at 3·2°K under 86 atmos. and at 1·1°K under 23 atmos. The solidification point of helium has not yet been definitely established, but it is known to be within 1°K. Solid helium cannot be distinguished visually from the liquid and hence must have almost the same refractive index as the liquid.

Adiabatic expansion process. Although liquefying machines based on the Joule-Thomson effect are in extensive use in laboratories and commercial centres, they cannot be said to be quite satisfactory, as their efficiency is very low, about 15%. This is due to the inefficiency of the basic process itself. A certainly more efficient method of cooling is to make the compressed gas expand adiabatically doing external work. As soon as the fact that a gas should be cooled below its critical temperature in order to be liquefied was recognised, the method that was naturally thought of first was to allow a highly compressed gas to expand adiabatically, when it would be cooled considerably on account of the external work done in expanding.

Hence, even before Pictet devised the cascade process to liquefy oxygen, Cailletet, in 1877, was able to liquefy oxygen by the adiabatic expansion process. Oxygen was compressed to a pressure of 300 atmospheres in a strong capillary tube, cooled to −29°C by liquid sulphur dioxide boiling under reduced pressure and then the pressure was suddenly removed, when a mist of oxygen was formed which disappeared after a few seconds. Pictet compressed oxygen to a pressure of 500 atmospheres and cooled it to about −130°C by liquid carbon dioxide boiling under reduced pressure. Then on suddenly releasing the pressure, oxygen in the form of a white solid was obtained. In 1884, Wroblewski obtained a mist of hydrogen and in 1893, Olszewski produced liquid hydrogen in sufficient quantities, by cooling compressed hydrogen with liquid oxygen and then suddenly removing the pressure.

The adiabatic expansion method, though in itself quite efficient, was discontinuous and hence was not developed on a commercial scale, until Claude and Heylandt employed it for liquefying air in a novel way. The chief technical difficulty in constructing an apparatus for continuous liquefaction of gases by this method consisted in finding a suitable lubricant for the moving parts of the expansion cylinder, since the ordinary lubricants solidified at the low temperatures involved. Claude overcame this difficulty by using petroleum ether, which remains viscous up to even − 160°C as lubricant.

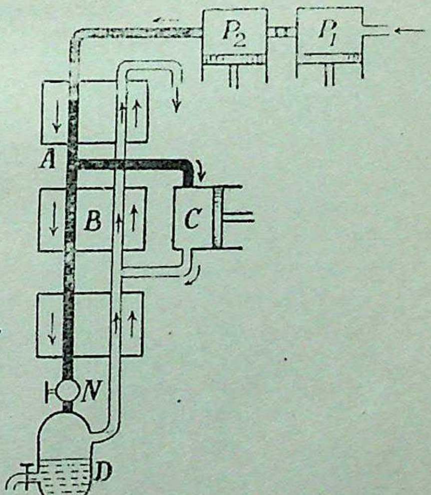
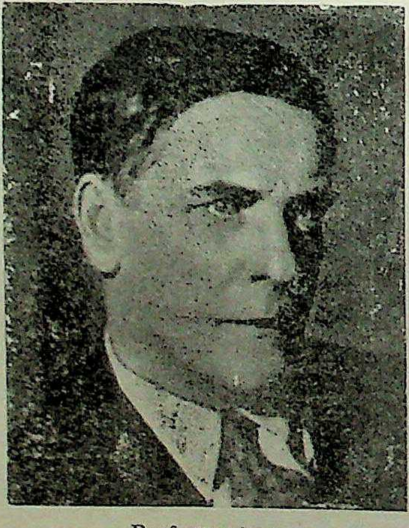


Fig. 172.
Claude's air liquefier.

Claude's air liquefier is shown in Fig. 172. Pure, dry air, compressed by the pumps P_1 and P_2, is divided into two parts at A. One part goes to the expansion cylinder C and suffers adiabatic expansion and consequent cooling. The cooled gas flows upward in the pipe B thereby cooling the second part of the incoming compressed gas in the second heat exchanger. The high pressure gas thus partially liquefies. It then suffers Joule-Thomson expansion at the throttle valve N. The liquid air is collected in a Dewar flask D. The evaporated air is taken to the compressor and again compressed.

Although, theoretically, Claude's method should be more efficient than Linde's method, in actual practice, it is only slightly so, evidently due to serious technical difficulties. The Linde's method has the great advantage that no movable parts of the apparatus are at low temperature. Heylandt made some slight improvements in Claude's liquefier.

It is of interest to note that Kapitza in 1934 employed Claude's method for liquefying hydrogen and helium. In 1947, Collins developed a commercial type of helium liquefier based on Kapitza's method, where a piston of nitrided nitralloy was used, thus eliminating lubrication of the movable parts.



Prof. Kapitza

Adiabatic demagnetisation. This method marks an important step forward in the attainment of the absolute zero. Before its advent, the lowest temperatures reached were those first of liquid helium (0·82°K) and then of solid helium (0·79°K), obtained by Kamerlingh Onnes and Keesom respectively. In 1926, Debye showed, on theoretical grounds, that still closer approach to the absolute zero was possible by the adiabatic demagnetisation of a paramagnetic salt. The process of magnetising a substance involves doing work on the substance, which will in consequence slightly rise in temperature. This result is known as the magneto-caloric effect. If a substance already magnetised is suddenly demagnetised, it will show a slight fall in temperature since it does work now and the required energy for it is drawn from within itself. According to the Curie law, the paramagnetic susceptibility of a substance is inversely proportional to the absolute temperature of the substance $\left(\chi \propto \frac{1}{T}\right)$. Assuming that this law holds good at the temperature of liquid helium, a paramagnetic substance will be powerfully magnetised at that very low temperature. If the substance is then adiabatically demagnetised, considerable cooling is produced, reaching a temperature lower than that of liquid helium.

This theoretical prediction was taken up for verification, in 1931, by Simon and Kurti, Giauque and McDougall, who devised an apparatus in which a paramagnetic salt, such as gadolinium sulphate, was first magnetised isothermally and then adiabatically demagnetised and the resulting temperature was carefully measured. Their experimental arrangement is shown in Fig. 173. The paramagnetic substance B (gadolinium sulphate) in the form of an ellipsoid or sphere of compressed powder is placed in a glass tube A, which is surrounded by Dewar flasks C, D and E, containing liquid helium, liquid hydrogen and liquid air respectively, as shown in the figure. This assembly is situated between the pole-pieces NS of an electromagnet.

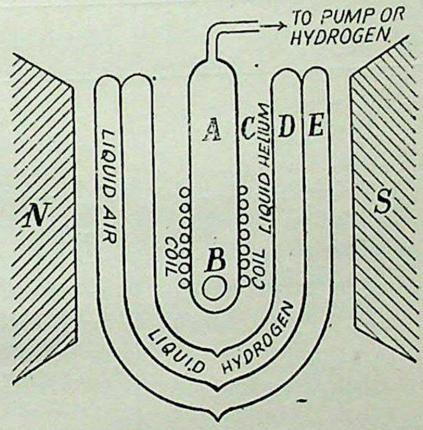


Fig. 173. Adiabatic demagnetisation.

The magnetic field of the order of 10,000 gauss is switched on and the specimen B is magnetised. The heat due to magnetisation is removed by first introducing hydrogen gas into A and then pumping it off with a high vacuum pump. In the meanwhile, the specimen picks up the temperature of liquid helium. Then the magnetic field is switched off when the substance is demagnetised adiabatically. The temperature of the salt is estimated by fitting a coaxial solenoid coil round the glass tube A and measuring the susceptibility at the beginning and at the end of the experiment. Giauque and McDougall were thus able to reach a temperature of 0·25°K, while de Haas, in 1944, working with a double sulphate of potassium and aluminium obtained a still lower temperature of 0·002°K.

Accessories employed in dealing with liquefied gases. (*i*) *Cryostats* are constant temperature baths used in low temperature work. The substance under investigation is kept immersed in such baths. The liquids to be used in cryostats depend on the particular range of temperatures desired and can be readily chosen from tables giving the normal boiling point, the critical temperature and the triple point of gases, as the one given here. The interval between the critical temperature and the triple point represents the range in which the liquid is available.

Substance	*Normal B.P.*	*Critical Temp.*	*Triple point*
Sulphur dioxide	− 10·1°C	157°C	...
Methyl chloride	− 24·1°C	143·3°C	− 103°C
Ammonia	− 33·4°C	131·9°C	− 77·7°C
Carbon dioxide	− 78·6°C	31·0°C	− 56·6°C
Ethylene	− 103·7°C	9·5°C	− 169°C
Methane	− 161·4°C	− 82·9°C	− 183·2°C
Carbon monoxide	− 190·0°C	− 138·7°C	...
Oxygen	− 183·0°C	− 118·8°C	− 218·4°C
Nitrogen	− 195·8°C	− 147·1°C	− 209·9°C
Hydrogen	− 252·8°C	− 239·9°C	− 248·7°C
Helium	− 268·8°C	− 267·8°C	− 259·1°C

(*ii*) *Dewar flasks* are essentially the same as the commonly used thermos or vacuum flasks. Such vessels are necessary to preserve low temperature liquids. They were first designed by Dewar. A Dewar flask, shown in Fig. 174, along with a low temperature syphon, consists of a double-walled glass vessel, the inter-space between the walls being completely evacuated and then sealed. The inner walls are silvered and polished. The silver polish protects the inside from radiation, while the vacuum between the two walls prevents passage of heat by convection and conduction through the walls. The mouth of the vessel is closed by a tight-fitting

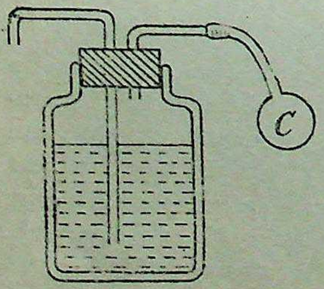


Fig. 174. Dewar flask.

stopper of a non-conducting material, like cork. Special syphons are used for drawing out low temperature liquids from a Dewar flask. They usually consist of double-walled tubes, with the space between the walls evacuated and the inside silvered. Applying a gentle pressure by means of a rubber compressor C, the liquid can be made to flow out through the syphon.

MEASUREMENT OF LOW TEMPERATURE

Liquid-in-glass thermometers can be used for measuring moderately low temperatures. Thus a mercury thermometer can be employed up to −38°C and an alcohol thermometer upto −111°C, while a special thermometer containing distilled petroleum ether down to −190°C. But these thermometers are not reliable for accurate measurement even in their respective ranges, on account of the many corrections to be applied.

Electrical resistance thermometers can be used for accurate measurement of low temperatures, provided the element used is perfectly pure, since pure metals show a regular variation in resistance with temperature. Fleming and Dewar found that the presence of even traces of impurity in a metal causes the thermometer to give inconsistent results at low temperatures. Henning found from a detailed investigation that the parabolic equation connecting resistance with temperature failed below − 40°C and hence suggested another relation of the form $R_t = R_0 (1 + \alpha t + \beta t^2 + \gamma t^3)$ for the range 0° to −193°C. For temperatures lower than −190°C, the platinum resistance thermometer can be used up to about 20°K, but there is no formula for deducing the temperature from the observed resistance. Onnes has employed lead and gold thermometers up to −259°C. For still lower temperature, constantan and phosphor-bronze have been employed ; but they all require a suitable formula for calculating the temperature.

Thermoelectric thermometers can be used for accurate measurement right down to very low temperatures. Copper-constantan and iron-constantan couples are very sensitive as they develop a comparatively large e.m.f. and can be used up to −255°C. Gold-silver couples have been used down to − 270·5°C. But the thermoelectric thermometers have to be calibrated by comparison with the standard gas thermometer.

Gas thermometers. The constant volume hydrogen or helium thermometer must be regarded as the standard instrument for low temperature measurement. Researches by Celozewski, Dewar, Onnes and others have greatly advanced the use of gas thermometers for accurate measurement in the low temperature range. Celozewski, by comparing thermometers containing oxygen, nitrogen, nitrous oxide with a hydrogen thermometer found that those thermometers could be used to measure temperatures close to their liquefying points. Dewar showed that the boiling point of hydrogen as indicated by the hydrogen thermometer was −253·0°C and −253·4°C, while a helium thermometer registered −253·7°C and −252·1°C. These results indicated that *a gas thermometer could be relied upon almost to its liquefying point.* Thus a helium themometer can be safely used right down to its boiling point, 4·2°K. But gas thermometers, from a practical point of view, are troublesome to work with, owing to their bulk, their slowness in adjusting themselves to the temperature of the bath, the precautions to be taken and the corrections to be applied.

Vapour pressure thermometers are most suited in the region below −254°C, and are indispensable for measuring temperatures below 4·2°K, the boiling point of helium. They are based on the *principle* that the vapour pressure of a liquid varies uniquely with the temperature. Hence measuring the vapour pressure of a liquid at the unknown temperature by means of a suitable apparatus, the temperature can be found using a calibration curve or a theoretical formula.

The liquids that are found useful for vapour pressure thermometers are sulphur dioxide, ammonia, carbon dioxide, etc. We shall describe here a *helium vapour pressure thermometer which is employed to measure temperatures below 4·2°K.* The instrument, shown in Fig. 175, consists of a small bulb A containing liquid helium and its vapour. The connecting tube is also filled with the saturated vapour of helium. A copper tube C surrounds the connecting tube to render the temperature uniform when a measurement

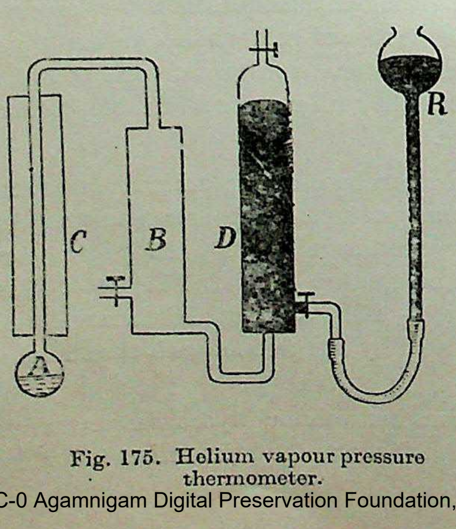


Fig. 175. Helium vapour pressure thermometer.

is made. By suddenly raising or lowering the mercury reservoir R, the vapour can be condensed or the liquid vaporised. The tubes B and D act merely as a manometer to measure the pressure of the saturated vapour. The helium vapour pressure thermometer has been used to measure temperature down to about 0·75°K.

Adiabatic demagnetisation thermometers. For measuring still lower temperatures the variation of the paramagnetic susceptibility of salts with temperature according to the Curie law is utilised. Since this law seems to hold good right up to the absolute zero, and the Curie scale agrees well with the absolute scale in known ranges, this method can be relied upon for such measurements (Cf. p. p. 426-7).

PRACTICAL APPLICATIONS OF LOW TEMPERATURE

The practical applications of the study of low temperature have turned out to be as fruitful as the theoretical investigations have been interesting. The important applications can be classified under two heads, *viz.*, in *pure* and *applied* sciences.

Applications in pure science. The extremely low temperatures, now made available by liquid air, liquid hydrogen and liquid helium, have opened a new and vast field of pure scientific researches. This has made it necessary for every modern laboratory to have at least a liquid air plant. Bottles of liquid air can be easily obtained at a comparatively low cost now-a-days. We shall first mention some of the important uses to which liquid air and other liquefied gases have been put and then consider a few interesting properties of matter discovered at very low temperatures.

Uses of liquid air and other liquefied gases. (*i*) *Preparation of oxygen and rare gases from liquid air.* The standard method of preparing oxygen on the commercial scale is by fractional distillation of liquid air. Since the boiling point of nitrogen is −195·8°C and that of oxygen −183°C, the portion that evaporates first will be rich in nitrogen while that evaporating last rich in oxygen. Hence a few fractional distillations will completely separate the two main constituents of air. Several rectifiers have been designed to obtain this separation.

Rare gases, such as helium, neon and argon, have also been isolated by the same process. Liquid air may be separated into two parts the more volatile consisting of helium, hydrogen and neon and the less volatile consisting of oxygen, nitrogen, argon, carbon dioxide krypton and xenon. Cooling the first part by liquid hydrogen will remove all others except hydrogen which can be subsequently removed by sparking with oxygen. Thus helium and neon may be obtained from atmospheric air.

(*ii*) *Calorimetry.* Dewar used calorimeters of liquid air, oxygen and hydrogen for researches on the specific heat of substances at low temperatures. Pure lead is used as the heater and the volume of the gas evaporated by the application of this heat is measured to determine the specific heat by the method of mixtures. These calorimeters have the advantage that a large amount of gas is formed which makes it possible to detect even very small quantities of heat. For example, with liquid hydrogen calorimeter 0·003 calorie of heat can be measured.

(*iii*) *High Vacuum* can be obtained by using liquefied gases. For example, if a vessel filled with a less volatile gas than air, such as sulphurous acid or water vapour, is surrounded by liquid air, all the gas inside becomes solidified and thus high vacuum is produced. If the vessel contains air, liquid hydrogen can be used to condense it and thereby produce high vacuum in the vessel. Presence of charcoal helps the process, since charcoal has the property of occluding gases at very low temperatures.

(*iv*) *Study of the upper atmosphere.* As we are now able to reproduce in the laboratory low temperatures and, therefore, conditions identical with those in the upper atmosphere, we can study its properties at leisure.

Properties of substances at very low temperature. (*i*) *At about —180°C and below chemical reactions do not take place* and hence putrefaction cannot happen, so that animal and vegetable matter are preserved intact. Bacteria and seeds are found to retain their germinative activity unimpaired even after exposure to liquid air temperatures, though a moderately high temperature kills them. Some materials like cotton, wool, leather, etc., begin to fluoresce after exposure to liquid air temperature. Lead becomes plastic at —190°C, while India rubber and glass become brittle.

(*ii*) *Physical properties also undergo wonderful changes at very low temperatures.* The atomic heat of all substances tends towards zero as the absolute zero temperature is approached. The magnetic susceptibility of paramagnetic salts varies almost inversely as the absolute temperature in the region of very low temperatures. The more striking changes are superconductivity and superfluidity, for which no satisfactory explanations are available yet.

Superconductivity. The electrical resistance of metals is found at ordinary temperature to vary almost proportionately with temperature so that one might expect it to disappear at absolute zero. But researches at very low temperatures have shown that this is not quite the case. Much before the absolute zero is reached, the resistance of metals decrease very rapidly and good conductors like copper have practically negligible resistance already at —230°C. Mercury, lead and tin lose their resistance altogether and that suddenly at 4·1°K, 7·2°K and 3·8°K respectively, when they are said to have reached the superconducting state. A current of 1,000 amperes passed for a long time through a thin wire of tin kept at 3°K does not produce any sensible heating of the wire, which, therefore, clearly indicates that the wire has no resistance. An electric current started inductively in a closed ring of lead at 7°K circulates undiminished for days. It is to be noted that not all metals have this superconducting state, but only some metals and alloys. Several theories have been proposed to explain the phenomenon, but none of them appears to be final.

Superfluidity. A more amazing phenomenon is met with liquid helium at about 2°K. Below 25 atmospheres pressure, helium is always a liquid, however low its temperature may be. In the neighbourhood of 2°K, the normal liquid known as *helium I* is suddenly converted into another, known as *helium II*. This new liquid experiences no resistance to flow through even the most narrow capillary tube ; in fact the narrower the bore, the more easily helium II flows through it. This is the reason for calling it *superfluid*, which represents a new frictionless state of matter, that also awaits an adequate explanation.

Industrial applications are many and varied. We have already mentioned the preparation of oxygen from liquid air on an industrial scale. Modern coal and mineral mines are furnished with a liquid air plant in order to have a plentiful supply of oxygen in the event of an explosion. Liquid oxygen is employed for preparing explosives by mixing it with powdered charcoal ; when the mixture is detonated, it explodes with great force. Passing over other similar uses, we shall consider somewhat in detail the two most common and useful appliances, *viz.*, *refrigerating* and *air-conditioning* machines.

Refrigerating machines are contrivances devised for the production of artificial cold required either to maintain a chamber for the storage of perishable food at a low temperature or to keep a brine-bath (*i.e.*, a bath containing a strong solution of calcium chloride) well below 0°C for the manufacture of ice.

The *basic principle* utilised in these machines is the cold produced by evaporation of a liquid under reduced pressure, often in conjunction with the cooling effect produced when a gas expands adiabatically, as already indicated.

The liquids ordinarily employed are ammonia, sulphur dioxide and more recently freon (CCl_2F_2), which are known as *refrigerants*. Ammonia is most commonly used in large refrigerating plants as in an ice factory, (hence called *ammonia plants*), while sulphur dioxide or freon is employed in small refrigerators meant for domestic purposes (called *frigidaires*). The choice of a suitable refrigerant depends upon the following factors. (*i*) The latent heat of vaporisation of the refrigerant liquid should be large which will allow a small quantity of it to produce the desired cooling effect. (*ii*) The refrigerant must be a vapour at N.T.P., but should be easily liquefied when compressed and cooled. (*iii*) The pressure of the vapour of the refrigerant liquid in the evaporator section maintained at about −15°C must be greater than the atmospheric pressure, so that impurities in the air may not get inside the apparatus and block the passage. (*iv*) The pressure required to liquefy the vapour of the refrigerant in the condenser section usually maintained at room temperature (30°C) should not be too great, otherwise there will be leakage of vapour and the compressor will have to be stout and heavy. (*v*) The specific volume of the vapour of the refrigerant should not be large, otherwise a very large compressor will be required. The table below gives the properties of the three refrigerants ordinarily used, which will make us realise their relative merits.

Substance	*Latent heat per lb. in B. Th. U. at −15°C*	*Normal boiling point*	*Cooling effect per lb. in B. Th. U.*	*Vapour pressure in lb./sq. inch at :—*		*Sp. volume of vapour in c. ft. per lb.*
				−15°C	30°C	
Ammonia	565·0	−33·4°C	474·5	34·3	9·2	8·15
Sulphur dioxide	175·6	−10·0°C	141·4	11·8	66·5	6·42
Freon	69·5	−30·0°C	51·1	26·5	107·9	1·49

It is seen that ammonia is the most suitable refrigerant. Sulphur dioxide can be more easily liquefied than ammonia and freon, so that a less stout compressor and condenser can be used, but for producing the same cooling effect as with ammonia, the compressor has to be made large.

Two types of refrigerating machines are in use, *viz.*, *compression* and *absorption* machines. The essential difference between the two consists in the manner of compressing the low pressure vapour : in the former a motor compressor is used, while in the latter a dilute solution of the refrigerant at room temperature is used to dissolve the low pressure vapour and the concentrated solution is heated to expel the vapour at high pressure. The compression type is more efficient, requires less initial cost and hence is used much more than the absorption type. The *electrolux refrigerator* is an absorption machine, while the *frigidaire* is a compression machine, both used for domestic purposes now-a-days. We shall describe these in greater detail, as typical of the two kinds of refrigerator.

The electrolux refrigerator. As stated above, the "electrolux" is an *absorption machine,* where the low pressure vapour is converted into high pressure vapour by means of an absorber. Ammonia is the most suitable refrigerant for use in this machine and water is chosen as the absorber, since water at 16°C absorbs about 1,000 times its volume of ammonia vapour, while if the ammonia solution is heated to 27°C ammonia vapour freely escapes from it.

The *principle of working* of an ammonia absorption machine is illustrated in Fig. 176. The generator G contains a strong solution of ammonia gas in water and is heated by a burner or some other means. Ammonia gas escapes from the solution and passes the

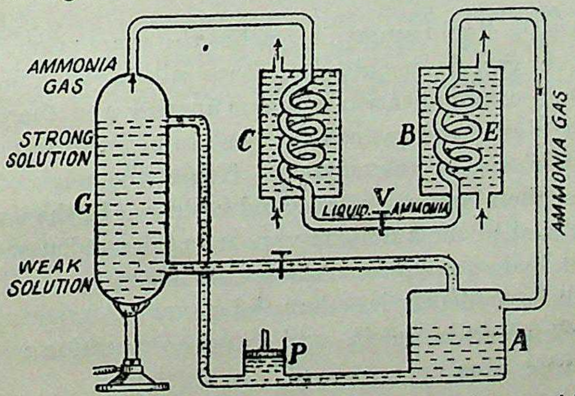


Fig. 176. Principle of action of ammonia absorption machine.

spiral immersed in the condenser C through which cold water is circulated. The gas condenses there under its own pressure into liquid ammonia. The liquid ammonia thus formed flows through a regulating valve V to the spiral in the evaporator E where it evaporates under low pressure, which is maintained by suitably adjusting V. The evaporator is kept in a brine-bath B as shown in figure, or in a chamber to be cooled. Since the liquid ammonia extracts the latent heat necessary for evaporation from the surrounding object, the brine-water or the chamber is thereby cooled. The ammonia gas resulting from the evaporation is led away to the absorber A containing water or dilute ammonia solution and thus the pressure in the evaporator is kept low. The solution in A gets concentrated and is passed on to the pump P which pumps it up to the generator at the top. Thus the supply of concentrated ammonia solution is maintained. Dilute ammonia solution from the bottom of the generator may be made to flow to the absorber to be concentrated there. Thus the cycle is repeated and the action is continuous, as long as cold water circulated in C and the supply of heat to G is maintained.

In the modern electrolux refrigerator, shown in Fig. 177, the valve V and the pump P are dispensed with, and the liquid ammonia is made to evaporate under reduced pressure by an ingenious application of Dalton's law of partial pressures, employing hydrogen gas, while the concentrated ammonia solution is transferred from the absorber to the generator by convection currents, instead of being pumped up. We shall now see how these improvements have been achieved.

When the liquid ammonia reaches the evaporator E, a stream of hydrogen gas flows into it. Since all parts of the circulating system are in communication with one another and there is only a slow flow of liquid and gas round it, the total pressure must be the same everywhere in the system. Hence the sum of the partial pressures of the ammonia vapour and hydrogen in the evaporator E is equal to that of the ammonia vapour in the condenser C. If there is sufficient hydrogen present, the partial pressure of the ammonia vapour will be evidently less than the saturation pressure in spite of the low temperature in E, and hence evaporation will take place under reduced pressure.

The mixture of hydrogen and ammonia gas, being heavier than hydrogen, sinks to the bottom of E and flows to the absorber A, where it meets a weak solution of ammonia in water. The ammonia gas gets dissolved at once in the solution due to its great affinity for water, while the hydrogen gas rises to the top and returns to E.

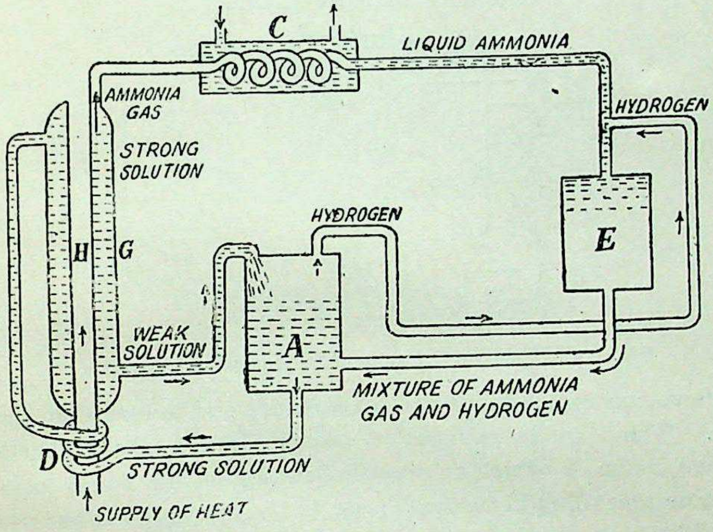


Fig. 177. Electrolux refrigerator.

The ammonia solution, which increases in strength, sinks to the bottom of A, and is made to flow into the generator G by convection currents due to the heat applied to it at D from the steam-pipe H which heats G. Thus the transfer of the strong solution from A to G is made in much the same way as in a central heating system.

Frigidaire is a *compression machine* where a compression pump driven by a motor is used to compress the low pressure vapour. Sulphur dioxide is commonly used as refrigerant in this type of machine.

The *principle of action* of a compression type of refrigerator is illustrated in Fig. 178. The refrigerant is compressed by the pump P driven by an electric motor or a steam engine. The cylinder of P has two valves Q and R, the former for the suction of the low pressure vapour from the evaporator E and the latter for the discharge of the compressed vapour to the condenser C. When the piston of the pump P moves upwards, the pressure in the cylinder falls below the pressure in the evaporator and as a result the valve Q opens and the low pressure vapour is sucked into the pump through the suction pipe. During the downward stroke of the piston, the vapour is compressed, which closes the valve Q and opens the valve

R, and the compressed vapour is delivered to the condenser through the discharge pipe. The condenser is cooled by circulating cold water

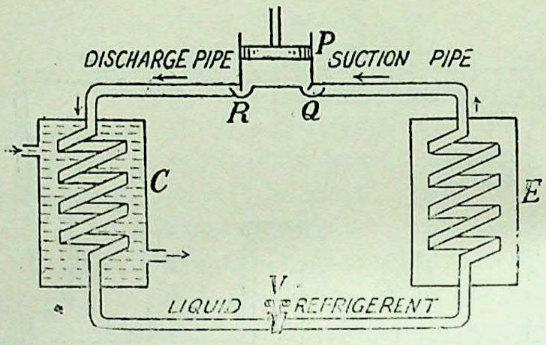


Fig. 178. Principle of action of compression machine.

and the vapour liquefies due to high pressure and lowering of temperature. The liquid refrigerant passes through the expansion or regulator valve V which reduces the pressure of the liquid from the high value prevailing in the condenser to the low value in the evaporator. Due to low pressure, the liquid evaporates in E, extracting its latent heat from the cold storage space or brine-water surrounding E. The space or brine-water is consequently cooled. The low pressure vapour is sucked in again by the compressor and the cycle of operations is kept up.

A modern type of frigidaire working automatically on the vapour compression principle is shown in Fig. 179. Liquid sulphur dioxide which is used as the refrigerant is contained in the evaporator coil E. As it evaporates, it extracts heat from the surrounding cold storage space which is thereby cooled. The low pressure vapour produced by evaporation collects at the top of E, and when strong enough it passes down through the suction pipe S and the crank case Q to operate the motor switch K. This starts the motor M, which works the compressor P compressing the low pressure vapour. The high pressure vapour is delivered through the discharge pipe D to the condenser C, which is cooled by a current of air forced across it by a fan mounted on M or by a flywheel F whose spokes are shaped like the blades of a fan. The high pressure vapour on being thus cooled condenses into liquid sulphur dioxide and collects in the tank T. From there, on account of the high pressure, the liquid is forced up through the liquid pipe L and enters E through a needle valve N. When sufficient amount of liquid has collected in E, a float valve V closes N. Thus the machine works only when the vapour pressure in E becomes large enough to operate the motor switch and the liquid is transferred from T to E only when the amount of liquid in E becomes so small that V

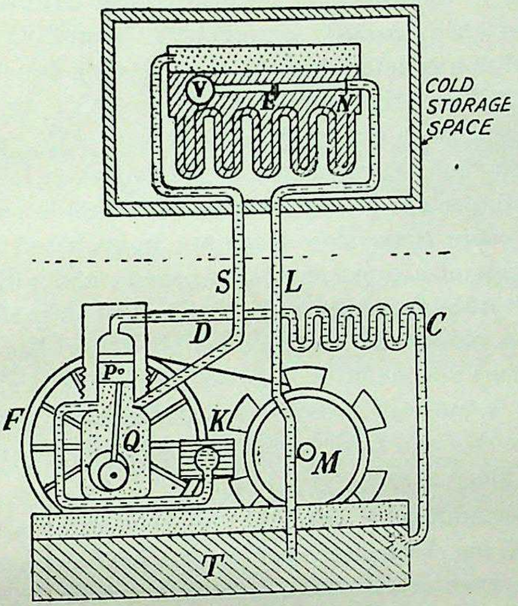


Fig. 179. Frigidaire.

sinks down to open N. Hence the operation is automatic.

It may be noted that in large refrigerating plants, as, for instance, in those used for making ice on a commercial scale, ammonia is used instead of sulphur dioxide. The evaporator coil is immersed in brine-water which is cooled well below 0°C without freezing. This brine-water is passed into a tank in which rectangular cans containing water are arranged ; the temperature of the brine-water being much below 0°C, the water in the cans is soon frozen into blocks of ice.

It may be noted also that there is a third type of refrigerator, called the *Bell-Coleman refrigerator*, largely used in ships for cold storage. It is of the *air compression* type, since air is used as the refrigerant, and the cooling effect is produced by allowing compressed air to *expand adiabatically*. An expansion cylinder will naturally replace the evaporator in this type of machine. The considerably cooled air from the expansion cylinder traverses the cold storage space, gets heated, returns to the compressor to be compressed and to begin a new cycle.

Air-conditioning machines. Air-conditioning may be defined as the art of controlling the weather within a limited space, such as a living room, so that one may feel comfortable in it, whatever be the conditions outside as regards temperature, humidity, etc. Average comfort condition is determined by the following factors :—temperature—75 to 77°F, relative humidity—60 to 65%, air movement—25 to 75 ft./min., fresh air circulation—at least 25%, purification of air, deodorizing and activating the air by ionisation. The first three are the most important factors, and special charts known as *comfort charts* and *effective temperature charts* are drawn based on the average comfort feelings of a great number of persons under different condition of temperature, humidity and air velocity. A perfect air-conditioning device must take into account all these factors. In cold countries, rooms are conditioned by electrical or central heating devices. In hot countries, however, air-conditioning primarily means keeping rooms cool and fresh, which is done by refrigeration. We shall speak of this alone here.

An air-conditioning machine is essentially a refrigerating machine which has been described in the previous section, with a difference, however, in the design of the evaporator. The evaporator in an air-conditioner consists of a series of zigzag copper tubes finned with thin copper plates in order to get a large area of cold surface. As the liquid refrigerant, sulphur dioxide or freon, evaporates in the tubes under low pressure, the tubes and fins get cooled. A fan put behind the evaporator drives the warm air through the cold fins and circulates the cooled air in the room. As the warm air passes through the cold fins the atmospheric moisture condenses on them into drops of water which can be drained away. Thus the high percentage of humidity in summer air is also brought down in the same process. The size and capacity of an air-conditioner depend not only on the *extent of the room*, but also on the *heat load*, which is determined by the heat conduction through walls and roof, the number of persons occupying the room, the entry of outside unconditioned air through doors and windows and the heat-producing items in the room, such as lamps, cookers, etc. In order to reduce the heat load which mostly comes from outside, the walls and roof are covered with badly conducting materials, such as masonite, celotex, etc. and the floor is matted. It is of interest to note that the new *rotocone system* has greatly improved the air-conditioning technique. It consists of a rotor built with a number of horizontal fins placed at an incline. As the rotor, arranged in front of the evaporator grill, rotates, cool air sweeps the entire room in an ever-widening cone, thereby eliminating stagnant layers of warm air and thus producing a feeling of freshness akin to natural air.

QUESTIONS

1. Describe Amagat's experiments on the compressibility of gases at high and low pressures. State his important conclusions. Indicate how the results can be explained with the help of the Van der Waals' equation. (*Madras University*)

2. Describe the experiments of Andrews on carbon dioxide. State and discuss the results obtained by him. Hence show that liquid and gaseous states are only distant stages of a long series of continuous changes. (*Bombay University 1953* ; *Baroda University 1954* ; *Punjab University, 1958*)

3. Give an account of Andrews' experiments on carbon dioxide. Indicate in a sketch, the form of the isothermals at 50°C, 31°C and 20°C. Explain their significance in relation to the liquefaction of gases and state the information they give on the behaviour of gases at high and low pressures. (*Madras University*)

4. What is meant by the critical temperature, critical pressure and critical volume of a gas ? How can these quantities be determined ? (*Cambridge*)

5. Define critical temperature, pressure and volume of a vapour and give some account of the behaviour of a substance near the critical point. (*Allahabad University*)

6. What is meant by the critical point in the state of a fluid ? Show on a diagram the character of typical isothermals of a fluid above and below the critical temperature. Explain how Van der Waals' equation accounts for the existence of a critical point. (*London B. Sc.*)

7. Distinguish between a gas and a vapour. Give an account of the variations from Boyle's law that exist in gases and vapours, illustrating your answer by typical graphs with pv and p as ordinates. (*Cambridge*)

8. Describe Holborn's experiments on the relation between the pressure and volume of a gas over an extended range of pressures. State the general nature of the results he obtained.

9. Write notes on :—
   (*a*) State of a substance near the critical point.
   (*b*) James-Thomson's hypothesis.
   (*c*) The law of corresponding states. (*Madras University*)

10. Discuss theoretically the production of cold by expansion of gases through porous plugs. How has this principle been applied in machines for liquefying air ? (*Allahabad University* ; *Delhi University 1953, 1954, 1959*)

11. Describe the porous plug experiment. Sketch a liquid air plant and explain its action. (*Madras University*)

12. Describe the porous plug experiment of Joule and Thomson and discuss the results obtained for different gases with special reference to hydrogen. Indicate how the results have been utilised for the liquefaction of air and hydrogen. (*Bihar University 1954 ; Punjab University 1954*)

13. What is Joule-Thomson effect ? Obtain the expression for the cooling produced assuming that the gas obeys Van der Waals' equation. Why do hydrogen and helium show a heating effect at ordinary temperature ? (*Allahabad University 1955 ; Rajasthan University 1960*)

14. Give an account of the methods of liquefying gases and discuss the principles on which they depend. (*Madras University ; Punjab University 1955 ; Tripos*)

15. Describe the methods employed in the liquefaction of (*a*) air and (*b*) hydrogen.

How are very low temperatures measured ? (*Cambridge University*)

16. Explain in brief outlines the reasons which led Van der Waals to his equation $(p + a/v^2)(v - b) = RT$. Discuss how far this equation is in keeping with experimental facts. (*Madras University ; Allahabad University 1950*)

17. Derive Van der Waals' equation of state and obtain expressions for the critical temperature, pressure and volume in terms of the constants of Van der Waals' equation. (*Calcutta University 1948 ; Patna University 1941 ; Aligarh University 1950 ; Bombay University 1953 ; Delhi Univerity 1953 ; Nagpur University 1953 ; Baroda University 1954 ; Punjab University 1957 ; Oxford ; Tripos*)

18. Explain the Van der Waals' equation of state and show how the constants in the equation can be determined in terms of critical constants.

Given that the critical pressure, temperature and volume of a gas are 73 atms., 31°C and 0·2066 of its volume at 0°C and 1 atm. respectively, calculate the constants of the Van der Waals' equation.

Ans. $a = 24{,}230$ atms., $b = 3{\cdot}505$ c.c./ gm. (*Madras University*)

19. Express the value of the critical temperature in terms of *a*, *b* and R. Calculate its value for CO_2 where $a = {\cdot}00874$ and $b = {\cdot}0023$.

Ans. $T_c = \dfrac{8a}{27Rb}$; $T_c = 32{\cdot}5°C$.

(*Allahabad University 1952 ; Punjab University 1957*)

20. Derive the reduced equation of a gas starting from Van der Waals equation of state. Show that if two gases have the same reduced pressure and volume, they also have the same reduced temperature. (*Punjab University*)

21. Discuss fully the methods for measuring low temperatures. (*Madras University*)

22. Explain why a vapour does not obey Boyle's and Charles' laws, and show how Van der Waals' equation allows for the two principal causes of divergence from these laws. (*Cambridge*)

23. What is meant by the critical temperature of a substance ? Explain the principle of the usual method of cooling air below its critical temperature. (*Cambridge*)

24. What is a refrigerator ? How many types of refrigerator are in use and how are they distinguished ? Describe in detail any one type of refrigerator.

25. Write notes on :—

(*a*) Refrigeration.

(*b*) Joule-Thomson effect.

(*c*) Temperature of inversion.

(*d*) State of a substance near the absolute zero.

(*e*) Adiabatic demagnetisation. (*I.A.S. 1953*)

(*f*) Van der Waals' equation.

(*Madras University ; Delhi University 1952, 1956*)

26. Describe fully one method of liquefying a gas. State clearly the principle underlying the method, and explain how the temperature of liquefaction may be measured. (*Cambridge*)

27. Give a critical account of the liquefaction and solidification of helium, paying special attention to the way in which the initial stages of the problem was tackled.

28. Describe and discuss the porous plug experiments of Joule and Kelvin.

Explain what is meant by temperature of inversion, illustrating your answer by reference to hydrogen and helium. (*London B.Sc.*)

29. Compare the results obtained in the porous plug experiment with air, hydrogen and carbon dioxide. What bearing has the above experiment on the methods used in liquefying gases ?

30. Give a critical account of the experiments carried out to see if the molecules of a gas attract one another and discuss the results obtained.

31. Distinguish between Joule-Kelvin cooling and adiabatic cooling.

(*Delhi University 1951*)

CHAPTER VIII

THERMODYNAMICS

Introduction. Thermodynamics, in a *literal* sense, is a branch of physics that deals with the relation between heat and mechanical energy. Its foundations were, in fact, laid by experiments in which mechanical energy was converted into heat, as in the researches by Rumford and Joule, and conversely heat converted into work, as in the steam-engines introduced between the times of Rumford and Joule. But in a *broader* sense, thermodynamics considers the relation of heat to other forms of energy also, such as electrical, magnetic, radiant, etc., since, as we know, these different forms of energy can be converted one into the other, consistent with the universal law of conservation of energy. The principles of thermodynamics are indeed very general in scope and have been widely applied not only to problems in physics but also to those in chemistry, such as chemical equilibria, electrochemistry, etc., and other branches of science, wherever heat plays a prominent part.

The study of all natural phenomena in which heat comes into action naturally falls under two heads, *viz.*, the study of *energy relations* and the study of *the manner in which energy changes take place*. Corresponding to those two investigations, thermodynamics presents itself in two forms, known as the *First and Second Laws of Thermodynamics* respectively.

The aim in this chapter is to study these two laws and apply them chiefly to various thermal phenomena, which have been considered in the preceding chapters.

THE FIRST LAW OF THERMODYNAMICS

The researches made by Rumford, Joule and others in support of the dynamical theory of heat, which have already been described in a previous chapter, form the experimental basis of the first law of thermodynamics. As we have seen, the results obtained in those rasearches can be analytically expressed by $W = JH$, which means that when a given amount of a work W is done, an equivalent amount of heat H is produced or when a certain quantity of heat H disappears an equivalent amount of a work W is always obtained, the equivalence being given by the constant J. This is the fundamental statement of the first law of thermodynamics, declaring the equivalence of heat and mechanical energy and thereby implying that heat is a form of energy like mechanical work. At once it appears that this law is merely a particular case of the general law of conservation of energy.

Clausius stated the first law of thermodynamics in a more comprehensive form as $dQ = dU + dW$, where dQ is the quantity of heat given to a system, dU the change in the internal energy and dW the external work done, J being omitted by expressing dQ in energy units (ergs). The quantity dU is defined with the help of the principle of conservation of energy by considering a thermally insulated system for which $dU = -dW$. Changes in the internal energy can thus be measured in terms of the external work on the system. The external work dW may be done in different ways. In the case of a simple gas expanding against a uniform external pressure p, $dW = pdv$; in elastic deformations $dW =$ stress × strain; work done against surface tension in the case of a liquid changing the extent of its surface is given by $dW = T\,ds$ where T is the surface tension; work done against electric and magnetic forces, $dW = V\,dq$ where V is the potential.

Although this law cannot be established by a rigorous mathematical proof it is to be considered infallible and any violation of it is impossible, since it is formulated directly from experimental observations.

Applications of the first law. In applying the first law to solve particular problems, it is to be borne in mind that the heat dQ added to the system cannot be determined by merely considering the initial and final states of the system, but the manner in which the heat is added must also be taken into account. Accordingly it is important to distinguish between the following different processes :—

(*i*) **Isothermal process**. Suppose a certain mass of a perfect gas undergoes an isothermal expansion by dv (*i.e.*, at constant temperature) against a constant pressure p; then the external work done $dW = pdv$. In an isothermal expansion from volume v_1 to volume v_2 under the same conditions, the total work done $W = p\,(v_2 - v_1)$. But if the pressure changes during the expansion, then the total work done is given by

$$W = \int_{v_1}^{v_2} p\,dv$$

But $pv = \mathrm{RT}$ or $p = \dfrac{\mathrm{RT}}{v}$

$$\therefore \qquad \mathrm{W} = \int_{v_1}^{v_2} \frac{\mathrm{RT}}{v}\, dv = \mathrm{RT} \int_{v_1}^{v_2} \frac{dv}{v}$$

since R is a constant and T also a constant in an isothermal process.

$$\therefore \qquad \mathrm{W} = \mathrm{RT} \log \frac{v_2}{v_1}$$

A graphical method of studying the same process, which is found very useful in the interpretation of the second law of thermodynamics, is known as an *indicator diagram*. Let us suppose a certain amount of the gas at a constant temperature undergoes changes in pressure and volume. These isothermal changes can be represented graphically by plotting the pressure against the volume, as shown in Fig. 180. Let the initial state of the gas be represented by the point A, its final state by the point B and the intermediate changes by different points on the line AB. Then the whole operation is represented by the line AB. Such a p-v diagram is called an *indicator diagram*.

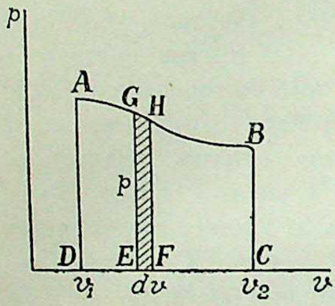


Fig. 180. Indicator diagram.

Considering an infinitely small expansion dv represented by EF at a pressure p represented by EG, the corresponding work done by the gas pdv is represented by the area of the shaded portion EGHF.

Now, the total work done by the gas in the change as it goes from A to B is evidently equal to the sum of all the areas similar to EGHF, *i.e.*, the area of ABCD or the area enclosed between the curve AB and the volume axis.

$$\text{Hence} \qquad \mathrm{W} = \int_{v_1}^{v_2} pdv = \text{area of ABCD}$$

Thus the indicator diagram gives directly the work done.

(*ii*) **Cyclic process.** In this process, since the system returns to its initial state $d\mathrm{U} = 0$. Hence $d\mathrm{Q} = pdv$ *i.e.*, the heat given to the system is equal to the external work done by it during the cyclic process. Thus we are able to obtain a direct relation between work done and heat absorbed, without the intervention of internal energy by making use of a cyclic operation, whose importance will be appreciated in the study of the second law of thermodynamics.

Considering the cyclic process graphically with the help of an indicator diagram, let us suppose that a given mass of a gas is taken through a series of changes in volume and pressure represented by ACB and BDA, so that it is brought back to the same conditions of pressure and volume as at start. (Fig. 181).

The external work done during the changes represented by ACB is given by the area ACBEFA. But this is not equal to the heat absorbed, since the internal energy of the gas is different at B from what it has been at A. Using the first law of thermodynamics, we may write

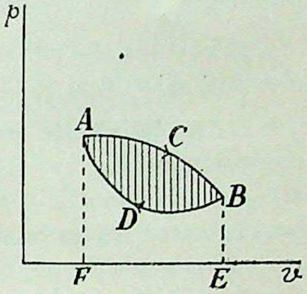


Fig. 181.

$$Q = (U_B - U_A) + \text{area ACBEFA},$$

where Q is the heat absorbed by the gas in going from A to B, and U_A and U_B are its internal energies at A and B respectively. If U_B is greater than U_A, some of the heat absorbed will go to supply this increase in internal energy, and in consequence the external work done will be less than the heat absorbed. But, since we know that the internal energy of any substance is fixed when its pressure and volume are specified, we may legitimately say *that the internal energy of a substance is always the same when its condition is represented by the same point on the indicator diagram.* Hence if the substance starts from a given condition of pressure and volume and is brought back to the same condition, its internal energy will be the same no matter what changes it may have undergone in the meantime. Referring to the figure, provided the gas starting from A is brought back to A, whether along BCA or BDA, its internal energy will not have changed ; but the same cannot be said of the external work done, since it is given by the area ACBEFA in the first case and by the area of ADBEFA in the second.

Applying the first law of thermodynamics to the whole cycle, the net amount of heat absorbed = the increase in the internal energy + the external work done.

But the increase in internal energy is zero, since the initial and final states of the gas are the same. Also the external work done by the gas in going from A to B through C is the area ACBEFA and that done *on* the gas in going from B to A through D is the area ADBEFA. Hence the net external work done by the gas in the whole cycle is the difference of these two areas, which is the shaded area enclosed by the cycle, ACBDA.

Therefore the net amount of heat absorbed = the external work done = the area enclosed by the cycle.

Thus the indicator diagram clarifies the nature of the heat absorbed dQ as well as of the external work done dW.

(*iii*) **Adiabatic process**. In this process, since the system is thermally insulated so that no heat can enter or leave the system, $dQ = 0$. Hence $dU + pdv = 0$. It is to be noted that although no heat enters or leaves in an adiabatic process, the heat content of the system does not remain constant during the change; on the contrary, it will be altered since the external work accompanying the change has to be drawn from the heat energy of the system. Further, in a strictly adiabatic process the system departs only by an infinitesimal amount from equilibrium with the external forces acting on it, so that the change is *reversible.*

The *work done*, when a certain mass of a perfect gas undergoes adiabatic changes in pressure and volume, the volume changing from v_1 to v_2, is given by

$$W = \int_{v_1}^{v_2} pdv$$

But $pv^{\gamma} = k$ (a constant) or $p = k/v^{\gamma}$ for adiabatic changes (*Cf.* p. 143).

$$\therefore \quad W = \int_{v_1}^{v_2} \frac{k}{v^{\gamma}} \cdot dv = k\left\{\frac{v^{1-\gamma}}{1-\gamma}\right\}_{v_1}^{v_2} = \frac{k}{1-\gamma}\left\{{v_2}^{1-\gamma} - {v_1}^{1-\gamma}\right\}$$

Since $\qquad k = p_1{v_1}^{\gamma} = p_2{v_2}^{\gamma}$

$$W = \frac{1}{1-\gamma}\left\{p_2{v_2}^{\gamma} \cdot {v_2}^{1-\gamma} - p_1{v_1}^{\gamma} \cdot {v_1}^{1-\gamma}\right\}$$

$$= \frac{1}{1-\gamma}\left\{p_2v_2 - p_1v_1\right\} = \frac{1}{\gamma-1}\left\{p_1v_1 - p_2v_2\right\} \quad \dots (1)$$

If the temperature of the gas changes from T_1 to T_2 during the operations,

$$p_1v_1 = RT_1 \text{ and } p_2v_2 = RT_2$$

$$\therefore \qquad W = \frac{R}{\gamma-1}(T_1 - T_2).$$

The slope of the adiabatic is γ times the slope of the isothermal under the same conditions of pressure and volume.

The isothermal relation is $pv = k$.

Differentiating $pdv + vdp = 0$

$$\therefore \quad pdv = -\,vdp \text{ or } \frac{dp}{dv} = -\,\frac{p}{v}\,.$$

Since $\dfrac{dp}{dv}$ gives the slope, the slope of the isothermal $= -\,\dfrac{p}{v}$ ... (1)

The adiabatic relation is $pv^{\gamma} = k$

Differentiating, $v^{\gamma}dp + p\gamma v^{\gamma-1}dv = 0$

Or $vdp + p\gamma dv = 0$

$$\therefore \quad \frac{dp}{dv} = -\,\gamma\,\frac{p}{v}$$

Since $\dfrac{dp}{dv}$ gives the slope, the slope of the adiabatic $= -\,\gamma\,\dfrac{p}{v}$ ... (2)

Comparing (1) and (2),

$$\frac{\text{slope of the adiabatic}}{\text{slope of the isothermal}} = \frac{-\,\gamma\,\dfrac{p}{v}}{-\,\dfrac{p}{v}} = \gamma.$$

These special features of the adiabatic process can be obtained also by means of an indicator diagram. Representing graphically the adiabatic changes of pressure and volume of a certain amount of gas, let AB represent the whole operation, the volume corresponding to point A being v_1 and that corresponding to B v_2 (Fig. 182). Considering an infinitely small adiabatic compression dv, the corresponding change from H to G may be considered to take place in two stages, a rise of temperature by $(dT)_p$ at constant pressure along HM and another rise of temperature by $(dT)_v$ at constant volume along MG.

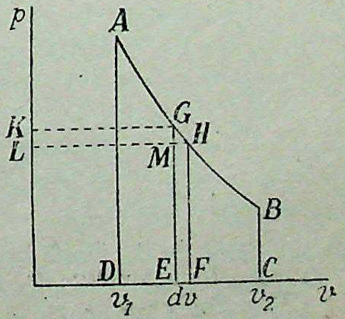


Fig. 162.

Since HM (= dv) and hence MG (= dp) are infinitely small, the two paths HG and HMG may be treated as coinciding.

Now, supposing the mass of the gas is 1 gm.,
the heat absorbed along HM = $C_p\,(dT)_p$
and the heat absorbed along MG = $C_v\,(dT)_v$
where C_p and C_v are the specific heats of the gas at constant pressure and constant volume respectively.

$\therefore$ Total heat absorbed $dQ = C_p\,(dT)_p + C_v\,(dT)_v$

But since the process is adiabatic, $dQ = 0$

$$\therefore \qquad C_p\,(dT)_p + C_v\,(dT)_v = 0 \qquad \ldots (1)$$

But $pv = RT$

At constant pressure, $pdv = R\,(dT)_p$

Or $(dT)_p = \dfrac{p}{R}\,dv$

At constant volume, $vdp = R\,(dT)_v$

$$(dT)_v = \frac{v}{R}\,dp$$

Substituting these values in (1)

$$C_p\,\frac{p}{R}\,dv + C_v\,\frac{v}{R}\,dp = 0$$

Dividing throughout by $C_v.pv/R$

$$\frac{C_p}{C_v}\cdot\frac{dv}{v} + \frac{dp}{p} = 0$$

Or $$\gamma\,\frac{dv}{v} + \frac{dp}{p} = 0$$

Integrating,

$$\gamma \log v + \log p = \text{constant}$$

Or $$pv^{\gamma} = \text{constant}$$

This is the gas equation which governs adiabatic changes, which we have already derived in another way (*Cf.* p. 143). This is an alternative method.

The work done, when the gas expands adiabatically by an infinitely small amount dv represented by EF, is given by the area of GHFE for reasons given in the analogous isothermal change (*Cf.* p. 446). The total work done by the gas in the adiabatic change as it goes from A to B is given by the area ABCD, *i.e.*, the area enclosed between the adiabatic curve AB and the volume axis.

$$\text{Hence } W = \int_{v_1}^{v_2} pdv = \frac{1}{\gamma - 1}\{p_1v_1 - p_2v_2\}$$
$$= \text{area of ABCD.}$$

Thus the indicator diagram here also gives directly the work done.

It can also be shown easily that the *slope of an adiabatic* is greater than that of the isothermal at the point where they cross on the indicator diagram. Let three isothermals of a gas at temperatures T, T + dT and T − dT be drawn, as shown in Fig. 183. Let us consider the adiabatic through the point B. If the gas expands adiabatically starting from the state represented by the point B, the external work done causes its temperature to fall and hence the adiabatic curve must descend to the T − dT isothermal and cross it at the point C, say. In a similar way, if it undergoes an adiabatic compression, its temperature rises and the adiabatic curve must ascend and cross the T + dT isothermal at the point A, say. Hence ABC is the adiabatic through B and its slope is greater than that of the isothermal at every point where they cross.

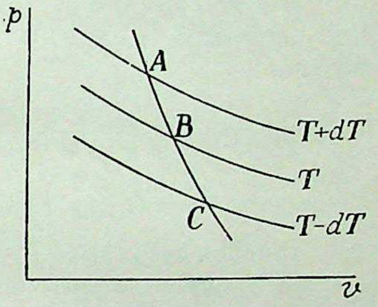


Fig. 183.

Having made these general considerations, let us take some particular applications of the first law of thermodynamics.

1. *Specific heat of a body.* The internal energy of a body depends entirely on its thermal state, which, in the case of a simple homogeneous body like a gas or a solid, is defined by its temperature T, pressure p or the volume v. Of these thermodynamic variables, only two are independent, the third being automatically fixed by the first two, since it is common observation that pressure, volume or temperature of a substance in any state, solid, liquid or gas, is perfectly definite when the other two quantities are known. Hence the internal energy U of a substance can be expressed by a relation of the form : $U = f(v, T)$ ... (1)

where U and v refer to a gram molecule of the substance.

Differentiating (1), we get

$$dU = \left(\frac{dU}{dT}\right)_v dT + \left(\frac{dU}{dv}\right)_T dv \qquad \dots (2)$$

[It may be noted that the quantity dU is a *perfect differential* of a function U of the variables defining the state of the substance.]

If a quantity of heat dQ is supplied to a thermodynamical system, part of it goes to increase the internal energy by dU while the remainder is spent in doing external work dW. We have from the first law of thermodynamics,

$$dQ = dU + dW, \quad \ldots (3)$$

where dQ and dU are expressed in energy units.

In *the case of a gas* expanding by a volume dv against a uniform external pressure p, $dW = p.dv$, so that the above relation (3) becomes

$$dQ = dU + pdv \quad \ldots (4)$$

Substituting for dU from (2) in (4), we get

$$dQ = \left(\frac{dU}{dT}\right)_v dT + \left(\frac{dU}{dv}\right)_T dv + pdv$$

Dividing both sides by dT,

$$\frac{dQ}{dT} = \left(\frac{dU}{dT}\right)_v + \left[p + \left(\frac{dU}{dv}\right)_T\right]\frac{dv}{dT} \quad \ldots (5)$$

Now $\frac{dQ}{dT} = C$, the gram-molecular specific heat. If the volume of the gas is kept constant,

$$\left(\frac{dQ}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v = C_v \quad \ldots (6)$$

where C_v is the specific heat at constant volume. If the pressure of the gas is kept constant,

$$\left(\frac{dQ}{dT}\right)_p = C_p \quad \ldots (7)$$

where C_p is the specific heat at constant pressure.

Taking account of these facts, relation (5) becomes

$$C_p = C_v + \left[p + \left(\frac{dU}{dv}\right)_T\right]\left(\frac{dv}{dT}\right)_p \quad \ldots (8)$$

For a *perfect gas*, we have :—

(*i*) $\left(\frac{dU}{dv}\right)_T = 0$, since there is no change in the internal energy during an isothermal expansion or compression, and

(*ii*) $p\left(\frac{dv}{dT}\right)_p = R$, since taking the relation $pv = RT$ and differentiating with respect to v and T, we get $p.dv = R.dT$ or $p\left(\frac{dv}{dT}\right)_p = R$.

Hence relation (8) in the case of a perfect gas becomes

$$C_p = C_v + R \text{ or } C_p - C_v = R \qquad \dots (9)$$

as has already been deduced (c. f. p. 141).

For *actual gases, liquids and solids* the relation is much more complicated.

2. *Latent heat.* When the temperature of a body (solid or liquid) is steadly raised, the body may suddenly change from solid to liquid state (fusion) or from liquid to gaseous state (vaporisation). In such discontinuous changes the energy also changes discontinuously. This is the phenomenon of latent heat. For instance, considering the vaporisation of 1 gm. of water at 100°C and 1 atm. pressure, the application of the first law of thermodynamics yields

$$L = u_2 - u_1 + p\,(v_2 - v_1)$$

where u_1, v_1 represent the internal energy and volume of 1 gm. of water and u_2, v_2 the corresponding quantities for the vapour.

The above relation indicates that the heat added is spent in two ways, first, converting 1 gram of water into 1 gm. of vapour having the same volume and secondly doing external work whereby the vapour expands under constant pressure to its specific volume.

$(u_2 - u_1)$ is called the *internal latent heat* and $p\,(v_2 - v_1)$ the *external latent heat.*

For water at 100°C, $v_1 = 1$ c.c., $v_2 = 1674$ c.c. (specific volume of saturated vapour)

$$\text{Hence } p\,(v_2 - v_1) = \frac{76 \times 13{\cdot}6 \times 980\,(1674 - 1)}{4{\cdot}18 \times 10^7}$$

$$= 40{\cdot}5 \text{ calories.}$$

Since $L = 539$ calories, the internal latent heat $(u_2 - u_1)$ is $539 - 40{\cdot}5 = 498{\cdot}5$ calories.

It may be noted that these thermal phenomena receive a more complete interpretation when the principles of thermodynamics are fully developed first and then applied to them.

THE SECOND LAW OF THERMODYNAMICS

The discovery of heat engines and their application to various industrial purposes may be considered as the starting point in the formulation of the second law of thermodynamics. *Carnot's theoretical researches on the ideal reversible heat engine,* belonging to this stage, paved the way for the recognition of the second law of thermodynamics as a law of Nature. The celebrated *enunciation of the law* by Kelvin and Clausius mark the second stage in the development of thermodynamics. Finally the restatement of the same law under a new concept called *entropy* by Clausius marks the last and triumphant stage where the law becomes one of the most fundamental in the whole of physical science. We shall, therefore, consider the second law of thermodynamics in four parts, *viz.*, heat engines, enunciation of the law in general with some simple applications, consideration of the law in terms of entropy and applications to particular problems.

HEAT ENGINES

Heat engines are contrivances for converting heat into work. From very early times it was observed that when bodies get heated they develop power. Thus, when water was boiled in a vessel whose mouth was closed with a lid, the lid was blown off by steam generated inside, which showed that high pressure steam could be made to do work. The use of wind for driving mills (wind-mills) and for propelling ships (sails) was based on the fact that high velocity wind could be made to do work. Such winds, as we know, are caused by intensive heating of parts of the earth by the sun. Similarly, explosives, such as gunpowder, were used for breaking rocks, projecting cannon balls, etc. These three rudimentary contrivances have been slowly but efficiently developed respectively into the modern *steam engines* used in locomotives, *gas turbines* employed in large electric power stations and in big ships, and *internal combustion engines* utilised in motor cars, aeroplanes, etc. Many of the physical principles used in these engines are common to all of them. Postponing their distinctive features and relative merits to a later section, we shall now consider only the essential features common to all of them that led to the discovery of the second law of thermodynamics.

A heat engine must have a hot body or *source* which can supply heat at a high temperature, a cold body or *sink*, into which heat is rejected at a lower temperature and a *working substance*, which can absorb heat from the source, convert some of it into external work by its expansion and reject the rest to the cold body. It is not possible to derive work from heat without a source and sink at different temperatures : at least no one has so far succeeded to do so. Also the conversion of heat into work always involves a drop in temperature of the working substance. A heat engine provides a continuous supply of work, because it is cyclical, *i.e.*, the working substance is taken through a cycle of operations which can be repeated indefinitely and thus the working substance is restored periodically to its original condition.

These essential features of a heat engine indicate that although any contrivance for transforming heat into work must rigorously obey the first law of thermodynamics and hence its efficiency $\eta = W/JQ$ must be unity in the ideal case, in actual realisation the efficiency is found small, about 5 to 55%, which means that at the most only 55% of the total heat energy supplied is converted into work. The question, therefore, naturally arises whether this low efficiency is due to the bad designing of the heat engines or whether there is something in the very nature of things which forbids converting the whole amount of heat into work. From the time of the invention of the steam engine by James Watt in 1765, attempts were made to increase the efficiency of heat engines, by a progressive improvement of technique, but it was found that one could never reach the mark imposed by the first law. A French engineer, Sadi Carnot, in the early part of the 19th century proved that *even with an ideal engine it was not possible to convert more than a certain percentage of heat into work, as a consequence of a law of Nature.* He also showed how the operations of a heat engine should be carried out in order that the efficiency might be maximum. We shall now see how he was able to establish these points.

S. Carnot

The Carnot ideal engine. An ideal heat engine, free from all the imperfections of actual engines and hence never realised in practice, was conceived by Carnot for theoretical investigation as follows. The ideal engine consists of :—

(*i*) a cylinder with perfectly non-conducting walls but with a perfectly conducting bottom containing a perfect gas as the *working substance* and fitted with a perfectly non-conducting and frictionless piston.

(*ii*) a hot body of high thermal capacity maintained at a constant high temperature $T_1°$ absolute to serve as the *source* of heat.

(*iii*) a similar cold body maintained at a constant lower temperature $T_2°$ absolute to be used as the *sink*, and

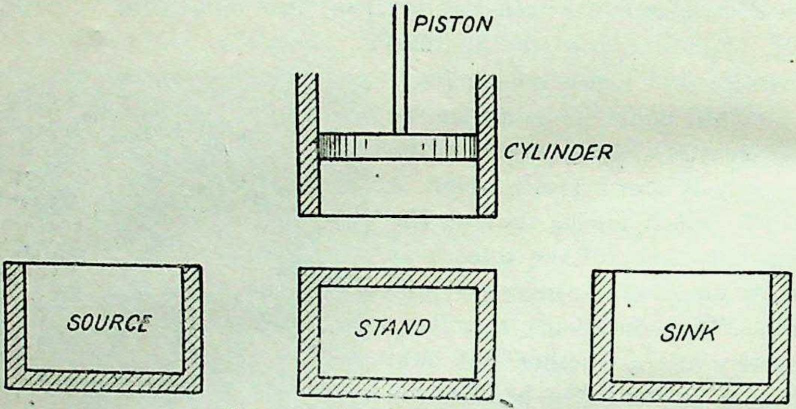


Fig. 184. Carnot's ideal engine.

(*iv*) a perfectly non-conducting platform to serve as a *stand* for the cylinder. (Fig. 184).

This ideal engine has to be worked in a special way in order that it may provide a continuous supply of power, which is known as the Carnot cycle.

The Carnot cycle. The gas in the cylinder is subjected to a series of operations constituting a complete cycle as follows :

(1) Let the initial temperature of the gas be T_1°K, the same as that of the source. Let the cylinder be placed on the source and the piston moved slowly so that the gas expands. This would make the gas fall in temperature, but as it is in contact with the source it can absorb the required heat to expand isothermally at the constant temperature T_1. This operation is represented by the isothermal curve AB on the *p-v* indicator diagram (Fig. 185). Let the amount of heat absorbed in this process be Q_1. By the first law of thermodynamics, Q_1 is equal to the work done w_1 by the gas in free expansion from a pressure

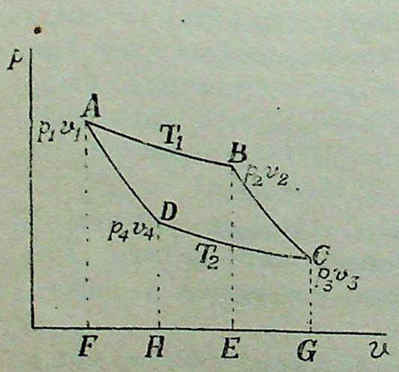


Fig. 185. Indicator diagram of Carnot's cycle.

p_1 and volume v_1 at A to a pressure p_2 and volume v_2 at B.

$$\therefore\ Q_1 = w_1 = \int_{v_1}^{v_2} p\,dv = RT_1 \log \frac{v_2}{v_1} = \text{area ABEF} \qquad \dots (1)$$

(2) The cylinder is removed from the source, placed on the perfectly insulated stand and the piston is allowed to move further so that the gas expands adiabatically till its temperature falls to T_2°K. This expansion of the gas is represented by the adiabatic curve BC on the indicator diagram. If p_3, v_3 be the pressure and volume of the gas at C, then the work done w_2 by the gas is given by

$$w_2 = \int_{v_2}^{v_3} p\,dv = \frac{R\,(T_1 - T_2)}{\gamma - 1} = \text{area BCGE} \qquad \dots (2)$$

Since the pressure of the gas is now very much reduced, in order to make it recover its capacity for doing work, it must be brought back to its original condition. To achieve this the gas is compressed in two stages, first isothermally and then adiabatically as follows :—

(3) For the isothermal compression the cylinder is removed from the insulated stand and placed on the sink maintained at the temperature T_2°K. The piston is moved very slowly so that the gas is compressed until its pressure and volume become p_4, v_4 represented by the point D. The heat developed owing to compression will pass to the sink, so that the change takes place at the constant temperature T_2. This isothermal compression is represented the curve CD on the diagram. The amount of heat Q_2 absorbed by the sink during the process is equal to the work done w_3 on the gas to compress it from p_3, v_3 state at C to P_4, v_4 state at D.

$$\therefore\ Q_2 = w_3 = \int_{v_4}^{v_3} p\,dv = RT_2 \log \frac{v_3}{v_4} = \text{area DCGH} \qquad \dots (3)$$

(4) The cylinder is removed from the sink and placed again on the insulated stand. The piston is lowered further so that the gas is compressed adiabatically until the temperature rises to T_1 and the gas attains its initial pressure and volume p_1, v_1. This adiabatic change is represented by the curve DA on the diagram. The work done w_4 on the gas during this operation is given by

$$w_4 = \int_{v_4}^{v_1} p\,dv = \frac{R\,(T_1 - T_2)}{\gamma - 1} = \text{area ADHF} \qquad \dots (4)$$

From (2) and (4), it is seen that $w_2 = w_4$ $\qquad \dots (5)$

The net work done by the gas $= w_1 + w_2 - w_3 - w_4$

$$= w_1 - w_3$$

$$= \text{area ABCD}$$

The net amount of heat absorbed by the gas $= Q_1 - Q_2$

$$\therefore \qquad Q_1 - Q_2 = w_1 - w_3 \qquad \dots (6)$$

This result could have been written down directly from the first law of thermodynamics as applied to a cyclic process, (*Cf.* p. 448).

The **efficiency** *of the engine* is given by

$$\eta = \frac{\text{heat converted into work}}{\text{heat drawn from the source}}$$

$$= \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \qquad \dots (7)$$

To express the *efficiency in terms of the temperature of the source and sink,*

$$\frac{Q_1}{Q_2} = \frac{w_1}{w_3} = \frac{RT_1 \log \frac{v_2}{v_1}}{RT_2 \log \frac{v_3}{v_4}} = \frac{T_1 \log \frac{v_2}{v_1}}{T_2 \log \frac{v_3}{v_4}} \qquad \dots (8)$$

Since the points B and C lie on the same adiabatic,

$$T_1 v_2^{\gamma - 1} = T_2 v_3^{\gamma - 1} \qquad (Cf. \text{ p. } 143)$$

where γ is the ratio of the specific heats of the working substance.

$$\therefore \qquad \frac{T_1}{T_2} = \left(\frac{v_3}{v_2}\right)^{\gamma - 1} \qquad \dots (9)$$

Similarly, since the points D and A lie on the same adiabatic,

$$T_1 v_1^{\gamma - 1} = T_2 v_4^{\gamma - 1}$$

$$\text{Or} \qquad \frac{T_1}{T_2} = \left(\frac{v_4}{v_1}\right)^{\gamma - 1} \qquad \dots (10)$$

Comparing (9) and (10),

$$\frac{v_3}{v_2} = \frac{v_4}{v_1} \text{ or } \frac{v_2}{v_1} = \frac{v_3}{v_4}$$

$$\frac{\log \frac{v_2}{v_1}}{\log \frac{v_3}{v_4}} = 1$$

Substituting this in (8)

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\therefore \qquad \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1} \qquad \dots (11)$$

This relation (11) shows that the efficiency depends only upon the temperature of the source and sink and is always less than unity, since $T_1 > (T_1 - T_2)$. The greater the difference between T_1 and T_2 the greater will be the efficiency.

The efficiency may be expressed also in terms of another quantity, which is known as the *adiabatic expansion ratio,* represented by the symbol ρ.

Considering the two adiabatics BC and DA,

$$\frac{v_3}{v_2} = \frac{v_4}{v_1} = \frac{1}{\rho}$$

Hence taking relations (9) and (10);

$$\frac{1}{\rho} = \frac{v_3}{v_2} = \frac{v_4}{v_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} \text{ or } \frac{T_2}{T_1} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

$$\therefore \quad \eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \qquad \ldots (12)$$

Reversibility of Carnot's cycle. A reversible process is one which can be retraced in the opposite direction so that it passes through exactly the same states in all respects as in the direct process. An essential condition of a reversible process is that the opposing forces are infinitely close to equilibrium which is secured by the process taking place infinitely slowly ; hence such a process may be considered as a quasi-static process, consisting essentially of a succession of equilibrium states. Any process in which these conditions are not satisfied is irreversible. Examples of reversible processes are :—(*i*) the transfer of heat between two bodies which are at the same temperature. If the bodies are at different temperatures, the transfer of heat occurring by conduction or radiation cannot be reversed and the process is irreversible ; (*ii*) a very slow extension or contraction of a spring, so that the work done upon the spring in stretching is equal to the work done by the spring while contracting at each step ; any fast stretching of the spring may set up vibrations in which part of the work will be spent thereby producing irreversibility ; (*iii*) infinitesimal changes of pressure or volume of a gas either abiabatically or isothermally, so that the amounts of work done during a balanced expansion or contraction are equal ; hence sudden unbalanced expansion or contraction of a gas, either isothermal or adiabatic, will be an irreversible process. Other clear examples of irreversible process are : (*i*) heat produced by friction, (*ii*) Joule-Kelvin effect, (*iii*) heating of an electrical resistance, (*iv*) diffusion of liquids or gases. It may be noted that while a reversible process can be represented by a line on the indicator diagram, an irreversible process cannot be so represented.

Applying these general principles to *Carnot's ideal engine*, it is easily seen that it is *perfectly reversible* on account of the total absence of all friction between the piston and the cylinder, the extreme slowness of the operations performed on the gas, the strictly constant temperatures under which the isothermal changes are made by the use of a perfectly conducting base for the cylinder and of a source and sink with an indefinitely large capacity and the prevention of loss of heat by conduction from the gas to the piston and cylinder by employing perfectly heat insulating material for the piston and the walls of the cylinder.

With such an arrangement, the *Carnot's cycle becomes reversible* at each stage, *i.e.*, instead of abstracting the heat Q_1 from a source at T_1 and transferring a part of it Q_2 to a sink at T_2 and converting the net amount of heat $(Q_1 - Q_2)$ into work, one can proceed in the opposite way where the machine abstracts the heat Q_2 from the sink at T_2; then work is performed on the machine and Q_1 is transferred to the source at T_1. In terms of the indicator diagram, this reverse process is achieved by performing the cycle in the opposite direction ADCBA, *i.e.*, first allowing the gas to expand adibatically from A to D with the cylinder placed on the insulating stand, then allowing it to expand isothermally from D to C in contact with the sink at T_2, the heat Q_2 being extracted in the process; then the gas is compressed adiabatically with the cylinder on the insulating stand till the point B at temperature T_1 is reached and finally the gas is further compressed isothermally till the point A is reached in contact with the source at T_1, the heat Q_1 developed in the process being transferred to the source at the higher temperature T_1 (Fig. 185). The machine, therefore, now acts as a *refrigerator*, *i.e.*, by doing work on it, it is made to extract from a colder body at T_2 the heat Q_2.

It is now evident that Carnot's reversible engine is only ideal which cannot be realised in practice. All the same it can serve as a standard by which the performance of actual heat engines can be judged.

Carnot, having thus established the possibility of a perfectly reversible engine capable of performing reversible cycles, proceeded to show that no engine can be more efficient than the perfectly reversible engine, the nature of the working substance being immaterial. This is known as the *Carnot's theorem*, of fundamental importance to the formulation of the second law of thermodynamics.

Carnot's theorem, may be stated thus : *The efficiency of a perfectly reversible engine is maximum and is independent of the nature of the working substance.*

The theorem can be proved by the following considerations :—

Suppose we have two heat engines A and B, A being reversible and B irreversible (Fig. 186). *If possible let B be more efficient than A.* Suppose B absorbs the heat Q from the source, converts a part W into work and rejects the rest Q — W into the sink. Let B be coupled to A and used to drive A in the reverse direction so that A acts as a refrigerator. Hence A abstracts a certain amount of heat from the sink, has the work W′ performed on it and returns the same heat Q to the source. The amount of heat A abstracts from the sink must then be equal to Q — W′. Now since B is assumed to be more efficient than A, W > W′ and hence Q — W′ > Q — W. This means that A abstracts more heat from the sink than B restores to it. The net result is that the compound engine AB abstracts (W — W′) heat per cycle from the sink and converts the whole of it into work, since the source is unaffected.

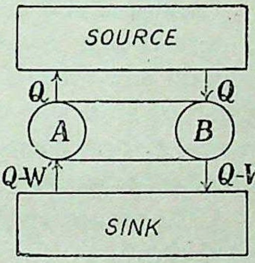


Fig. 186.

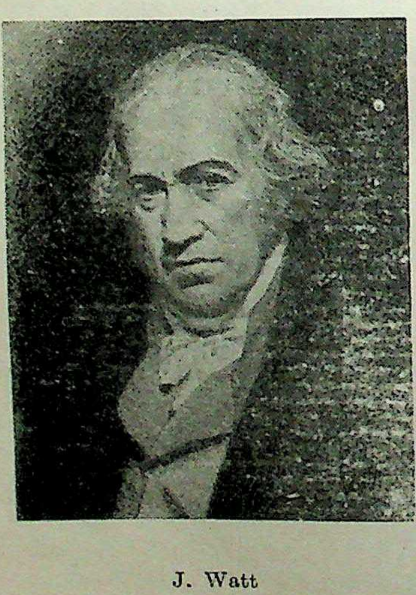
Thus a compound arrangement of two engines is able to draw heat from a body continuously and convert the whole of it into work without producing any change in other bodies. This would be splendid, indeed, since there is an unlimited amount of heat in the air, ocean, etc., and if this process were feasible, one can get work without any expenditure of energy by the use of some sort of a perpetual motion machine. But no one has ever succeeded to do such a thing so far, *i.e.*, to derive work from heat from a single body without the intervention of at least another body at a higher temperature. Such being the human experience, one is obliged to conclude that the assumption by which the impossible conclusion is reached, *viz.*, the efficiency of the irreversible engine is greater than the reversible one must be untrue. In other words, *no engine can be more efficient than the reversible engine, whose efficiency, therefore, is maximum.* This is the same as stating that the *efficiency of all* *reversible engines working between the same two temperatures is the same.*

Again, assuming that a reversible engine using a particular working substance is more efficient than another reversible engine working with a different substance, it can be shown by a similar argument as above that such an assumption leads to the same absurd conclusion. Hence, *whatever be the nature of the working substance, the efficiency is the same for all reversible engines* working between two given temperatures.

Thus Carnot's theorem is proved.

Study of the actual heat engines in use. After having thus established that reversibility is the ultimate criterion of efficiency, we may now proceed to consider briefly the different kinds of heat engines in use and study their relative merits. As already indicated, the modern heat engine can be classified under three heads, *viz.*, the *steam engine*, the *internal combustion engine* and the *gas turbine*.

The steam engine. The modern type of steam engine was first designed in 1765 by James Watt, a scientific instrument maker at Glasgow. Although he is usually given the credit of the discovery of the steam engine, he made use of very important findings by other workers before him, such as, for instance, the use of *high pressure steam* for pumping water from wells by Thomas Savery in 1698, the introduction of *safety valves* for regulating the high pressure steam by Papin about the same time and the very important invention of the *cylinder and the piston* for operating on the working substance, made by Newcomen in 1705 in connection with his atmospheric engine. James Watt, after a series of investigations on the discoveries of his predecessors, refined their techniques before incorporating them and introduced new contrivances, such as a separate condenser, the double stroke system, the governor and the throttle



J. Watt

valve, the crank, the eccentric and flywheel, which gave the steam engine its present efficient form.

The **essential parts of the steam engine** are shown in Fig. 187. S is the steam chest which supplies steam to the cylinder C through a slide valve V. P is the piston which works smoothly inside C. The piston rod K is attached through a connecting rod L to a mechanism consisting of a crank H, shaft G, a flywheel F and an eccentric E, by means of which the to-and-fro motion of the piston is converted into circular motion of the wheels attached to the shaft (not shown in the figure). As the piston works, the connecting rod pushes the crank which thereby rotates the shaft. The flywheel F keeps the rotation of the shaft continuous due to its large moment of inertia, in spite of the 'dead centres' where the connecting rod and the crank being in the same line, the former cannot push the latter. The eccentric E is a disc mounted on the shaft eccentrically and works the slide valve V, thereby synchronising the rotation of the shaft with the movement of the piston. The boiler where steam is generated and the condenser into which the residual steam is ejected from the cylinder are not shown in the figure. Likewise, an automic device, consisting of a governor and throttle valve, and geared to the shaft, which controls the supply of steam from the boiler into the steam chest and thereby ensures smooth running of the engine at a constant speed, is not shown.

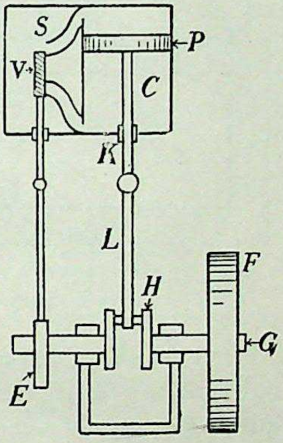


Fig. 187. Essential parts of a steam engine.

The **principle of working** of the steam engine is illustrated in Fig. 188. Steam at high pressure enters the steam-chest S through a pipe A. In the position shown in the figure, steam enters the cylinder C through the opening B at the right and pushes the piston P forward towards the left, thereby driving the low pressure steam in front through C to the exhaust D. As the piston moves forward the slide valve moves back and closes B. When the piston has moved still farther, the steam in the cylinder is subjected to an adiabatic expansion, the forward stroke being thus completed. The temperature and pressure of the steam having fallen considerably due to the adiabatic expansion, the piston moves backward, aided by the entry of high pressure steam into the cylinder through the opening C at the left. During this backward stroke the piston drives the low pressure steam in front to the exhaust D through B, and the slide valve moves forward to close C eventually. Steam entering the cylinder through C is subjected to a similar complementary cycle of operations, so that the to-and-fro motion of the piston is made continuous.

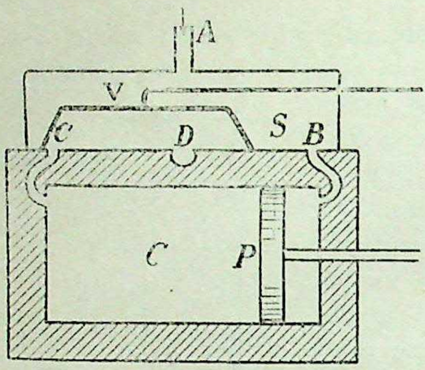


Fig. 188. Principle of working of a steam engine

The use of high pressure steam enables the *expansive power of steam* to be utilised with advantage. Cutting off the steam when the piston has moved some distance, the piston will complete its journey by the expansive power of steam, whose pressure will in consequence be very much reduced. Thus more work is obtained from the same amount of steam by allowing the steam to expand adiabatically and hence the running of the machine is made more economical.

To achieve this successfully, the use of *a separate condenser* is necessary. For, the expansive power of steam depends upon its temperature. Now when the steam enters the cylinder which has been previously cooled to create a vacuum, some heat is taken up by the cylinder, so that the temperature of the steam falls and its expansive power consequently diminished. Watt, observing that a large part of the expansive power of steam was lost on account of the alternate cooling and heating of the cylinder, introduced a separate condenser, and to keep the cylinder always hot he further surrounded it by a steam box.

Since the time of Watt, many improvements have been made in the steam engine, but the essential features remain the same. In the modern steam engines, steam of much higher pressure than that used by Watt is regularly employed. The high pressure steam is not allowed to expand completely in a single cylinder, but the expansion is spread out in three or four cylinders. The condenser consists of a number of tubes containing cold water kept in circulation and provided with a pump to transfer the water resulting from condensation of steam to the boiler.

The **efficiency of the steam engine.** In the steam engine the working substance is a mixture of water vapour and water produced by the two isothermal operations of evaporation and condensation respectively. If the Carnot cycle is performed on such a working substance as with perfect gas, the result obtained will be as shown in Fig. 189. AB represents the process of evaporation to produce steam by boiling water under a high but constant pressure and at a temperature T_1. BC represents the adiabatic expansion of steam in the cylinder, when the pressure and temperature are considerably reduced. CD corresponds to the condensation of the steam ejected into the condenser which takes place isothermally at a lower but constant pressure and at a lower temperature T_2. Actually all the steam will become water, but to complete the Carnot cycle, the condensation must be arrested at some point D before all the steam is condensed. DA represents the adiabatic compression which brings the working substance back to its original state.

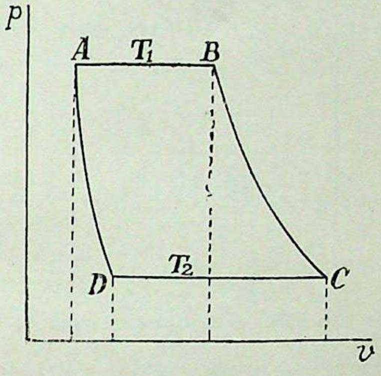


Fig. 189. Carnot cycle for the steam engine.

If such a cycle could be performed with a steam engine, its efficiency, according to Carnot's theorem, would be the same as with a perfect gas. But such a thing is not possible, since the condensation along CD is far too quick to leave any steam for the adiabatic compression along DA, chiefly given the fact that the condenser forms a separate unit from the cylinder. Hence the cycle employed in a steam engine is modified into what is known as the Rankine cycle.

The **Rankine cycle** is represented by the indicator diagram in Fig. 190. The first three operations represented by AB, BC and CD are the same as in the Carnot cycle detailed above. The fourth and final operation represented by DA consists in transfer of water produced by the condensation of steam from the condenser to the boiler by means of a pump. The work done by a steam engine performing the ideal Rankine cycle is represented by the area ABCD. All steam engines strive to conform to this cycle, but there are many practical difficulties to be overcome. For instance, there is always a drop of pressure when steam enters the cylinder from the boiler ; the adiabatic expansion is never completed before the condensation starts ; the mechanical valves do not function instantaneously, and so on. Hence actual steam engines attain to only 60 to 70% of the efficiency of the ideal Rankine cycle and their indicator diagrams have the corners of ABCD rounded off. The calculation of the efficiency of the ideal Rankine cycle from a knowledge of the equation of state of steam is complicated and hence a simpler method is used in engineering practice, into the details of which we shall not enter here.

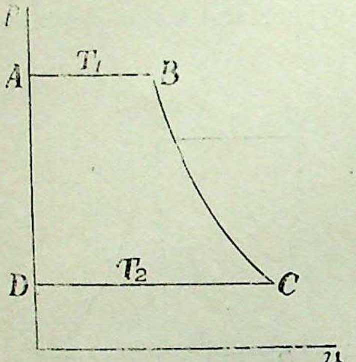


Fig. 190. The Rankine cycle.

The internal combustion engine. In this type of heat engines, the hot source is produced by the explosion of a mixture of air and some combustible gas like petrol vapour, atmosphere forming the condenser and air the working substance. It is called *internal combustion engine,* because in it heat is produced by the combustion of fuel *inside* the cylinder, whereas a steam engine, in which heat is produced *outside* the cylinder in a separate boiler, may be considered as *external combustion engine.* There is another essential difference between steam and internal combustion engines, *viz.*, in the former heat is absorbed by the working substance *at constant temperature,* while in the latter *at constant volume* or *constant pressure.* The internal combustion engine is much more efficient than the steam engine, since the working substance can be heated to a much higher temperature. There are two kinds of internal combustion engines, known as the *Otto engine* and the *Diesel engine* ; in the former petrol vapour is used as fuel, whereas in the latter a crude oil (Diesel oil) supplies the fuel. These two kinds are more scientifically distinguished by the different cycles employed, *viz.*, the *Otto cycle,* in which the heat is absorbed by the working substance at *constant volume* and the *Diesel cycle* where the heat is absorbed at *constant pressure.* The majority of the internal combustion engines in use is of the Otto type. We shall now briefly study the two kinds of internal combustion engines and compare their action and relative merits.

The Otto engine consists of the usual cylinder and piston, the cylinder being provided with inlet valves for air and petrol vapour and exhaust valves. The operations of these valves are controlled by the motion of piston. The working substance is air and petrol vapour acts as fuel.

The **principle of working** is illustrated in Fig. 191. The Otto cycle first employed successfully by Otto, a German engineer,

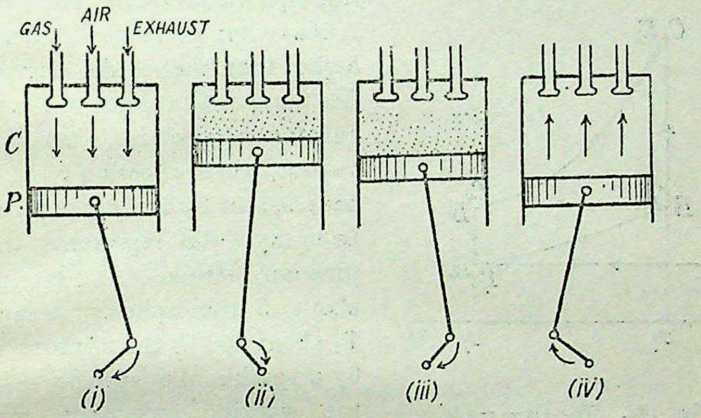


Fig. 191. The four strokes of the Otto engine.

in 1876, consists of four operations, known as *strokes*.

(*i*) *The charging stroke.* The inlet valves are open and a suitable mixture of air and petrol vapour is sucked into the cylinder C by the forward motion of the piston P.

(*ii*) *The compression stroke.* All the valves are closed and the mixture is compressed adiabatically to about 1/5 of its original volume by the backward motion of the piston. The temperature of the mixture is hereby raised to about 600°C. The process is called *pre-heating*. At the end of the compression stroke, the mixture is fired by a series of sparks from a sparking plug. The combustion causes a large amount of heat to be developed which raises the temperature of the gas to about 2000°C and a corresponding high pressure (about 15 atmospheres) is produced instantaneously.

(*iii*) *The working stroke.* The piston is now driven forward with great force owing to the high pressure of the gas, and the gas expands adiabatically to the original volume with a corresponding drop of temperature.

(*iv*) *The exhaust stroke.* At the end of the third stroke, the cylinder is filled with a mixture of gases which is useless for further work. The exhaust valves are then opened and the spent up mixture is ejected out of the cylinder, the piston moving backward. After this scavenging of useless gases is completed, a fresh charge of air and petrol vapour is sucked in and a new cycle starts.

The four operations described above are represented on the indicator diagram in Fig. 192. EA represents the charging stroke, in which the mixture is sucked in at atmospheric pressure. The mixture at A is at a temperature T_1°K, not much higher than that of the surrounding. Let the specific volume of the working substance (which is air, not the petrol vapour, whose function is to merely heat the air by its combustion) at A be v_2 say. AB represents the compression stroke. At B (pressure about 5 atmospheres, temperature T_2 about 600°C) the mixture is fired by a spark ; the specific *volume* of the working substance remaining *practically constant*, say at v_1, there is an instantaneous large increase of pressure and temperature to T_3 (15 atmospheres and 2000°C). This change is represented by BC. CD represents the working stroke during which the gas expands adiabatically to the original volume v_2 with a consequent drop of temperature to T_4. At D the exhaust valve is opened and the pressure falls to the atmospheric pressure shown by DA. AE represents the exhaust stroke.

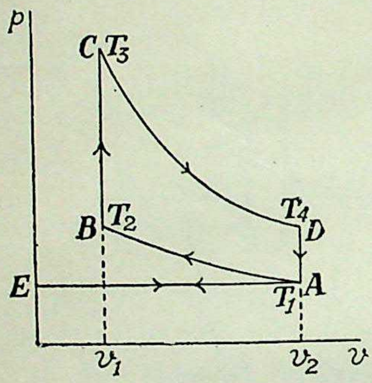


Fig. 192. The Otto cycle.

The **efficiency** of this engine can be obtained as follows :— Considering 1 gram of the working substance, the heat Q_1 supplied to it by combustion is given by

$$Q_1 = C_v (T_3 - T_2)$$

where C_v is the specific heat at constant volume.

The heat Q_2 rejected is given by

$$Q_2 = C_v (T_4 - T_1)$$

Hence the efficiency

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad \ldots (1)$$

Since AB is an adiabatic process,

$$T_1 v_2^{\gamma-1} = T_2 v_1^{\gamma-1}$$

where γ is the ratio of specific heats of the working substance.

$$\therefore \qquad \frac{T_1}{T_2} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} \qquad \dots (2)$$

Similarly, since CD is an adiabatic,

$$T_3 v_1^{\gamma-1} = T_4 v_2^{\gamma-1}$$

$$\text{or} \qquad \frac{T_4}{T_3} = \left(\frac{v_1}{v_2}\right)^{\gamma-1} \qquad \dots (3)$$

$$\therefore \qquad \frac{T_4}{T_3} = \frac{T_1}{T_2} = \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

Using this result in (1)

$$\eta = 1 - \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

Since $\frac{v_2}{v_1}$ is the adiabatic expansion ratio ρ,

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \qquad \dots (4)$$

where $\frac{1}{\rho}$ is called the *adiabatic compression ratio.*

Thus we obtain for the efficiency of the Otto cycle an expression similar to that obtained in the Carnot cycle (*Cf.* p. 459). Then why not use the Carnot cycle, since it has maximum efficiency ? But in designing an engine, other practical considerations must be taken into account, besides theoretical efficiency. In the first place, it is desirable to have a machine which is fast-working, *i.e.*, in which the cycle of operations is completed as quickly as possible. This rules out the Carnot engine since it absorbs the required heat by a comparatively slow isothermal process, while the Otto engine acquires the heat by a much quicker adiabatic process. Secondly, the maximum pressure developed in the Carnot engine also forbids its use in practice. For instance, between the same two temperatures 2040°K and 340°K, the Carnot engine develops a maximum pressure of 1178 atmospheres, while the Otto engine only 27 atmospheres, although the efficiency of the former will be 83%, while that of the latter only 45%. This reduction in efficiency in the Otto engine is more than compensated by its design being much more compact, less heavy and stout than the Carnot engine, which has necessarily to be very bulky and heavy to withstand the very high pressure developed, so that its power output will be extremely small compared to its bulk.

The Diesel engine. Diesel, another German engineer, not satisfied with the low efficiency of the Otto engine and investigating the possibility of arriving at the efficiency of the Carnot cycle by some contrivance or other, produced another engine, which was more efficient that the Otto type, though it could not reach that of the Carnot type. Since the efficiency η depends on the expansion ratio ρ as given by the relation

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

if ρ is increased, η also will increase. But in the Otto engine ρ cannot be increased beyond a certain value (about 5), otherwise the mixture will be spontaneously ignited during compression before the spark passes. Hence Diesel designed an engine in which no fuel is introduced until the compression is completed.

The Diesel engine consists of a cylinder and piston, the cylinder being much more robust than in the Otto engine, since it has to withstand a higher maximum pressure (about 35 atmospheres). The cylinder is provided with inlet valve for air, the working substance, another inlet through which a heavy crude oil acting as fuel can be sprayed into the cylinder at the right moment and exhaust valves. The operations of these inlets and outlets are controlled by the motion of the piston.

The **principle of working** is shown in Fig. 193 and the Diesel cycle, consisting of five operations or strokes, in Fig. 194.

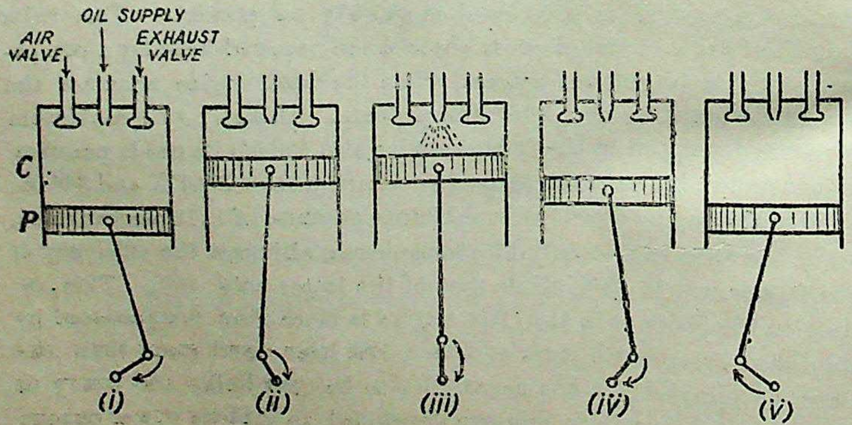


Fig. 193. The five strokes of the Diesel engine.

(*i*) *The suction stroke.* The air-valve is opened and pure air is sucked into the cylinder at constant pressure (atmospheric). This is represented by EA on the indicator diagram (Fig. 194).

(*ii*) *The compression stroke.* All the valves are closed and the air is compressed to about 1/17th of its original volume. The temperature rises to about 1000°C and the pressure to about 35 atmospheres. AB on the indicator diagram represents this operation.

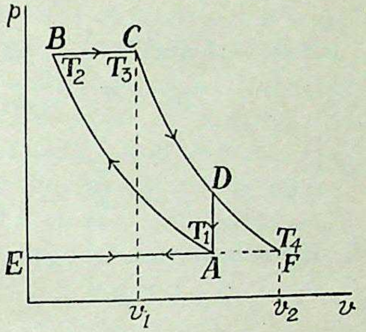


Fig. 194. The Diesel cycle.

(*iii*) *The injection of oil.* The supply valve is opened and oil under pressure is sprayed into the cylinder. The oil burns spontaneously as the temperature in the cylinder is much above its ignition point. The *pressure* during this process is maintained *constant* by regulating the oil supply. This is represented by BC. Due to combustion, the temperature rises to about 2000°C. At this stage the oil supply is cut off.

(*iv*) *The working stroke.* All the valves are closed. The gas mixture is allowed to expand adiabatically, the piston moving forward, until the curve CD is described. Strictly speaking the mixture must be allowed to expand freely until the pressure drops to the original value represented by F ; but as this would involve a large volume for the cylinder, in actual practice, the exhaust valve is opened at a stage represented by D and the pressure drops to A.

(*v*) *The exhaust stroke.* The useless spent up gas mixture is forced out. This is represented by AE. The machine then becomes ready for the next cycle.

The **efficiency** of this engine may be calculated as follows. We shall first consider the ideal cycle CFAB. Let the specific volumes and pressures of the working substance at C and F be v_1 and v_2, and p_2 and p_1 respectively. Let T_1, T_2, T_3 and T_4 be the temperatures at A, B, C and F respectively.

Considering 1 gm. of the working substance, the heat supplied by combustion of the fuel along BC is given by

$$Q_1 = C_p \ (T_3 - T_2)$$

where C_p is the specific heat at constant pressure.

The heat rejected outside along FA is given by

$$Q_2 = C_p (T_4 - T_1)$$

The efficiency $\eta = 1 - \dfrac{Q_2}{Q_1} = 1 - \dfrac{T_4 - T_1}{T_3 - T_2}$ ... (1)

Since A and B lie on the same adiabatic,

$$p_1^{1-\gamma} T_1^{\gamma} = p_2^{1-\gamma} T_2^{\gamma} \quad \ldots (Cf. \text{ p. } \quad)$$

Or $$\frac{T_1}{T_2} = \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}} \quad \ldots (2)$$

Similarly, since C and F lie on the same adiabatic,

$$p_2^{1-\gamma} T_3^{\gamma} = p_1^{1-\gamma} T_4^{\gamma}$$

Or $$\frac{T_4}{T_3} = \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}} \quad \ldots (3)$$

Comparing (2) and (3)

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} = \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{p_2}{p_1}\right)^{\frac{1-\gamma}{\gamma}}$$

Again since C and F lie on the same adiabatic,

$$p_2 v_1^{\gamma} = p_1 v_2^{\gamma}$$

Or $$\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^{\gamma}$$

$$\therefore \quad \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{p_3}{p_1}\right)^{\frac{1-\gamma}{\gamma}} = \left(\frac{v_2}{v_1}\right)^{1-\gamma}$$

Substituting this in (1)

$$\eta = 1 - (\rho)^{1-\gamma} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots (4)$$

Thus we have for the efficiency the same formula as for the Carnot or the Otto cycle.

Relation (4) gives the efficiency for the ideal cycle, where heat would be rejected at constant pressure along FA. Actually, however, the exhaust valve is opened at D and heat is rejected at constant volume along DA. Hence

$$Q_2 = C_v (T_4 - T_1),$$

taking the temperatures at D and E to be practically the same.

For the actual Diesel cycle, therefore,

$$\eta = 1 - \frac{C_v(T_4 - T_1)}{C_p(T_3 - T_2)} = 1 - \frac{1}{\gamma}\left(\frac{1}{\rho}\right)^{\gamma-1} \qquad \ldots(5)$$

The efficiency for the ideal cycle can be calculated and is found to be about 63%. The efficiency for the actual cycle is, therefore, somewhat lower, about 55%. Even with this lower value, the Diesel engine is more efficient than the Otto engine ; also it consumes less and cheaper fuel. But it must be more robustly built to withstand higher pressure and is beset with much greater mechanical difficulties, which have been, however, successfully overcome. All things considered, it must be said that the Diesel engine is a decided improvement on the Otto engine.

During the past fifty years the internal combustion engines have been greatly developed and have supplanted the steam engines, which consume much more fuel, in several cases. Some of the modern means of transport such as the automobile and aeroplane would not have been possible, but for these internal combustion engines. The Otto engine is usually employed for motor cars and aeroplanes while the Diesel engine for driving ships. Now-a-days, motor trucks and buses as well as locomotives also employ Diesel engines.

The gas turbine, which has been evolved from the time-honoured wind-mill, is a modern machine, in which a graded change of momentum of a gas is used to produce rotary motion. Steam is the gas that has been commonly employed for a long time, although in recent models high-pressure gases replace steam, resulting in greater efficiency.

A gas turbine is rightly classed among the heat engines, because it works on the same basic principle. A gas raised to a high pressure and temperature enters a system of blades constituting the turbine which it drives round by executing an adiabatic expansion, and then leaves the turbine to be exhausted into the condenser at a lower temperature, to which it rejects the heat which it has not been able to convert into work. But a special feature of the gas turbine is that the heat energy of the gas is first employed to set the gas itself in motion inside fixed nozzles and this kinetic energy is used to do work on the blades of the turbine. The nozzles are so designed that the heat energy is most efficiently converted into mechanical energy, so that a *constant jet* is produced. We shall now consider the theory of formation of such a jet in the case of a steam turbine.

Theory of steam jets. Let steam be made to travel through a fixed nozzle from a region of high pressure A to a region of low pressure B. (Fig. 195). Let p_1, v_1, u_1 and x_1 be the pressure, volume, internal energy and velocity respectively of steam in A and p_2, v_2, u_2 and x_2 the corresponding quantities in B.

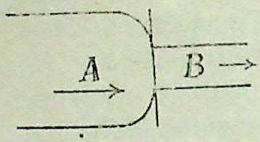


Fig. 195.

The next work done on steam as it traverses the nozzle $= p_1v_1 - p_2v_2$, and the loss in internal energy $= u_1 - u_2$. The gain in kinetic energy of steam per gram on traversing the nozzle $= (x_2^2 - x_1^2)/2J$ calories.

Assuming that the process is adiabatic, from the first law of thermodynamics, we get

$$\frac{1}{2J}(x_2^2 - x_1^2) = p_1v_1 - p_2v_2 + u_1 - u_2 = H_1 - H_2$$

where $H_1 - H_2$ is the heat drop.

As the initial velocity is practically zero, *the kinetic energy of the issuing jet is given by the heat drop $H_1 - H_2$.*

Assuming that there is no loss of heat energy through friction or eddy currents in the nozzle, *i.e.*, under ideal conditions, the heat drop $H_1 - H_2$ is due to an adiabatic process where the pressure drops from p_1 to p_2, which can be readily obtained from steam tables. This presents maximum work obtainable from a steam turbine under most favourable conditions.

A gas turbine is also a product evolved from its prototype, the wind-mill, because the wind that turns the sails of a wind-mill is itself due to unequal heating of different parts of the earth's surface, so that the wind-mill is basically a heat engine. Since wind power is not always reliable, the steam turbine was invented, in which the motive power is *constantly* supplied by the artificial jet caused by high pressure steam traversing specially designed nozzles.

We shall now give a brief description of the two types of steam turbines which were first constructed, towards the end of the last century, known as the *impulse turbine* of De Laval and the *reaction turbine* of Parsons.

The De Laval turbine works on the following principle. The steam jet issuing from fixed nozzles with great velocity strikes on the blades of a turbine wheel and in passing through them has its direction changed and then escapes to the exhaust. This gives an *impulse* to the wheel which is thereby set in rotation. The action of the steam jet on the blades is illustrated in Fig. 196. The blades are parallel, so that they offer very little obstruction to the steam jet and hence the pressure of steam remains practically the same on both sides of wheel. The blades are fixed at the periphery of the wheel. As the steam jet impinges on the blades with very high velocity, in order that the blades may not be smashed due to the large centrifugal forces developed, De Laval designed the turbine wheel in a special way, very thick near the axis with a thin shaft so that it can safely bear the stresses set up by rotation.

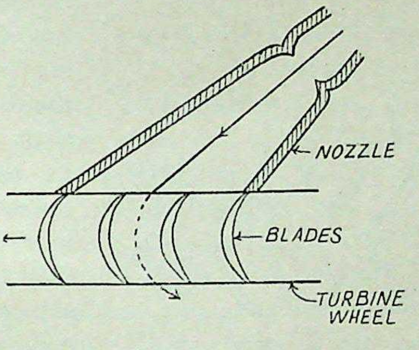


Fig. 196.

The De Laval turbine was designed, for reasons of safety, to produce low power. For generating high power, superheated steam must be used. This means the pressure drop in the jet will be very great and the blades will move with a correspondingly very high velocity, which is not safe. To overcome this difficulty, Curtis, Zolly and others adopted a device first employed by Parsons for his own turbine, which consists in distributing the huge pressure drop over a number of stages, each stage consisting of one set of nozzles and one ring of blades. The sets of nozzles and the corresponding rings of blades are all mounted on the same wheel. Since across each stage the pressure drop is small, the blade velocity necessary for maximum efficiency can be realised in practice within the limits of safety.

The Parsons' turbine works on the *redction principle, viz.*, the turbine wheel is set in rotation in the opposite direction by the reaction produced by a jet of steam issuing out of the blades set in the wheel. The essential feature of this turbine is the *distribution of pressure drop over a large number of stages, for which a special blading system is employed* as described below.

The reaction turbine of Parsons consists of a cylindrical case fitted with rings of *inwardly projecting* blades, (fixed blades) and a concentric shaft fitted also with rings but of *outwardly projecting* blades (moving blades), which lie between those in the case. The cylindrical case and the shaft are like the stator and rotor of an electric motor. The blades have convergent passages, *i.e.*, the passage narrows down towards the exit, as shown in Fig. 197. As the fixed blades act as nozzles, there are no separate nozzles for producing a jet.

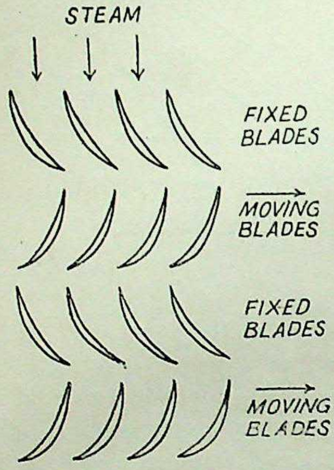


Fig. 197. The blading system of a reaction turbine.

Steam under pressure admitted parallel to the shaft enters a ring of fixed blades and issues as a jet, which passes into the next ring of movable blades. There is a drop of pressure, in consequence of which the jet increases in velocity as it traverses the blade passage, and as it issues out, a *backward reaction* is produced on the blades which consequently begin to rotate. The steam jet then passes through a second stage consisting of another pair of fixed and moving blades, imparting through reaction, increased rotational force on the rotor. The process is repeated at each of the stages, which may be as many as 50 or even 100. On account of the peculiar form of the blade passages, the pressure drop is spread over a large number of stages, so that the velocity of the jet is relatively small, well within safety limit, while the cumulative rotational effect on the rotor is kept high.

It may be noted that, as the jet enters the moving blades with some relative velocity giving it an impulse as in De Laval's turbine, Parsons' turbine really works partly by impulse, partly by reaction. As a matter of fact, all turbines are driven by reaction due to the change in the velocity of the jet in direction and magnitude. In the pure impulse type, the reaction is mainly due to the jet being slowed down, while in the pure reaction type, the reaction is due to the acceleration imparted to the steam in the moving blades on account of the pressure drop.

As already stated, in recent times, high pressure gases have been used instead of steam in the turbines. In the *internal combustion turbines*, the burning of some oil serves to heat the enclosed air to a high temperature and pressure, and the high pressure gas thus produced drives the turbine wheel.

The great advantages of gas turbines over the steam and the internal combustion engines are :—(*i*) the expansion of the gas can be made much more completely in the turbine than in the other engines, where the to-and-fro motion of the piston is involved. (*ii*) On account of the absence of this reciprocating motion in the turbine, a uniform rotatory motion is produced by a constant torque applied directly to the shaft, and all vibrations are minimised. (*ii*) The turbine requires considerably less space and is cheaper to construct. (*iv*) The turbine can bear greater overloading than the other engines of the same power. (*v*) Due to its capacity of generating large power, it is almost exclusively used in all large electric power stations and in big ships for propulsion.

The Wankel engine. The most recent advance made in this type of engines is the replacement of the linear piston by the rotary type. This modification was planned, designed and executed in 1957 by Herr Wankel of the research department of the German Automobile Company NSU (Neckarsulm Automobil Werk). A sports car fitted with this wonder engine, having only 500 c.c. capacity, but developing 50 H.P., has been exhibited during this year in the Frankfurt Automobile Show. The Wankel engine, popularly known as the 'wonder engine", is a rotation rear-engine that is cooled by a water-filled aggregate.

Mr. Wankel was dissatisfied with the "unreasonable technical detour" of the standard piston engine that converted the linear piston movement into a rotating one *via* crankshaft and connecting rod. He tried to construct a motor that would not necessitate these back and forth movements but would rotate from the start. After gaining the necessary practical and theoretical knowledge, he finally discovered the decisive factor that made construction of the surprisingly uncomplicated engine possible : an eight-sided structure, mathematically known as an "epitrochoid". This is formed when a triangle circles around its centre of gravity and simultaneously creates a circling movement. A triangular metal structure, the rotary piston, moves inside the engine according to the principle of circling and rotating. Due to the movement within the engine, the hollow space between the pistons and the outer wall continually change their volume, thus allowing their piston replacement to be used as any four-cycle engine.

The advantages of this amazing principle are :—(*i*) The engine has only two movable parts, (*ii*) makes much less noise than the piston stroke engine, (*iii*) uses considerably less space—the new motor is about as large as the palm of the hand, and (*iv*) weighs only a fraction of a normal engine.

The jet engine. During the Second World War, a new type of engine, known as the *jet propulsion*, has been developed, with the main idea of devising a powerful means of propulsion for high speed aircraft. It works on the *rocket principle*. A mixture of air and fuel is compressed and then ignited so as to obtain high pressure. The high pressure gas is made to escape at a very high velocity at the rear of the machine, which, on account of the reaction thus produced, moves forward with enormous velocity. The modern *"jet plane"* is thus able to fly at a speed even greater than that of sound. The very recent launching of the *"baby moons"* and *"sputniks"* to circulate round the earth marks the most up-to-date development of the jet propulsion system.

FORMULATION OF THE SECOND LAW OF THERMODYNAMICS

Carnot had established in connection with heat engines that it is impossible to convert heat completely into work and further that even for the partial conversion of heat into work heat must be extracted from a hot body and the portion not converted into work must be given up to the cold body, so that the flow of heat energy is entirely governed by the temperature, irrespective of the nature of the working substance. Clausius and Kelvin generalised this discovery of Carnot and stated it as a second fundamental law of thermodynamics.

Kelvin stated it thus :—*It is impossible to derive a continuous supply of energy by cooling a body below the coldest of its surroundings.* This can be readily understood from the fact that a *heat engine* cannot work already when the temperatures of the source and sink are equalised and much more so when the source cools down to a temperature lower than that of the coldest body in the surroundings.

Clausius stated the law in a different form thus :—*It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature, or heat cannot of itself pass from a cold to a hot body.*

This statement is equivalent to Kelvin's, but viewed in the opposite way. It is also easily understood from the fact that no one has ever produced a *refrigerator* that works without a supply of energy.

The second law, as stated in either way, cannot be proved *directly*, since it is negative in form; but it is accepted as a universally true experimental law, so that the discovery of an exception would be a sensation of the first order. It has been applied to a wider range of phenomena than any other single physical law, as for instance, change of state, solution, osmotic pressure, primary electric cell, thermoelectricity, chemical reactions, etc., and in every case its predictions, both qualitative and quantitative, have been verified by experiment.

It is important to note the distinction between the first and second laws. The *first law* asserts in general the equivalence between work and heat implying that mechanical energy and heat are only different forms of energy and *that mechanical energy can be completely converted to heat* by such processes as friction ; but it says nothing about the origin of the heat, whether it is a hot body or cold body, since both might equally serve the purpose. The second law goes a step further and imposes additional restrictions on the first law by asserting that *when heat is converted into work, only a partial coversion is possible* even under the best conditions and that any *such conversion essentially requires a hot body and a cold body simultaneously*.

Before we proceed to a more comprehensive study of the second law in terms of entroy, let us consider some simple but important applications of the law, *viz.*, the thermodynamic scale of temperature, latent heat equation, refrigeration and characteristics of a uniform temperature enclosure.

(*i*) **Thermodynamic or absolute scale of temperature.** In the study of the measurement of temperature, we have seen that all scales depending on the properties of particular substances, such as expansion of a liquid or gas, change in electrical resistance of platinum, etc., are arbitrary and disagree with one another, although the perfect gas scale depending on the properties common to gases in general rather than on those of one gas is in some measure satisfactory (*Cf.* Ch. I). With the introduction of the ideal heat engine, whose efficiency is entirely independent of the properties of any particular working substance, depending only on two temperatures, and the formulation of the second law, Kelvin realised the possibility of obtaining a non-arbitrary scale of temperature in terms of mechanical energy independent of the properties of any particular substance. He worked out the theory of such an *absolute* scale, known also as Kelvin's *work* or *thermodynamic scale,* and showed that it agreed with the perfect gas scale, as follows :—

Since the efficiency of all reversible engines working between any two temperatures θ_1 and θ_2 is a function of these two temperatures alone, we may write $\eta = f(\theta_1, \theta_2)$.

But
$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

where Q_1 is the amount of heat absorbed at the higher temperature θ_1 and Q_2 the amount of heat rejected at the lower temperature θ_3,- θ_1 and θ_2 being measured on any arbitrary scale.

$$\therefore \qquad 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

or
$$\frac{Q_1}{Q_2} = F(\theta_1, \theta_2) \qquad \ldots (1)$$

where F denotes some other function of θ_1 and θ_2, *i.e.*,

$$F(\theta_1, \theta_2) = 1/[1 - f(\theta_1, \theta_2)]$$

Similarly, if the reversible engine works between the temperatures θ_2 and θ_3, $(\theta_2 > \theta_3)$, we have

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3) \qquad \ldots (2)$$

and if it works between θ_1 and θ_3, $(\theta_1 > \theta_3)$

$$\frac{Q_1}{Q_3} = F(\theta_1, \theta_3) \qquad \ldots (3)$$

Multiplying (1) and (2)

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = \frac{Q_1}{Q_3} = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

Comparing this with (3)

$$F_1(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) \qquad \ldots (4)$$

If this relation (4) is to be satisfied, $F(\theta_1, \theta_2)$ must be of the form $\varphi(\theta_1) / \varphi(\theta_2)$, where φ is another function of temperature.

[Proof
$$F(\theta_1, \theta_2) = \frac{\varphi(\theta_1)}{\varphi(\theta_2)}$$

$$F(\theta_2, \theta_3) = \frac{\varphi(\theta_2)}{\varphi(\theta_3)}$$

$$\therefore F(\theta_1, \theta_2) \times F(\theta_2, \theta_3) = \frac{\varphi(\theta_1)}{\varphi(\theta_2)} \times \frac{\varphi(\theta_2)}{\varphi(\theta_3)}$$

$$= \frac{\varphi(\theta_1)}{\varphi(\theta_3)} = F(\theta_1, \theta_3)$$

which is relation (4)].

Therefore, for any reversible engine

$$\frac{Q_1}{Q_2} = \frac{\varphi(\theta_1)}{\varphi(\theta_2)} \quad \dots (5)$$

Since $\theta_1 > \theta_2$ and $Q_1 > Q_2$, $\varphi(\theta_1) > \varphi(\theta_2)$ which means that $\varphi(\theta)$ *is a linear function of* θ *and may be used to measure temperature.*

Representing, therefore, $\varphi(\theta)$ by τ, which would be some multiple of θ,

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2} \quad \dots (6)$$

This relation (6) can be used to define a new scale of temperature, which does not depend upon the properties of any particular substance. The ratio of any two temperatures on this scale is equal to the ratio of the heat taken in and heat rejected by an engine working reversibly between the two temperatures. Hence it is called the *absolute* or *thermodynamic scale.*

Relation (6) can be written as

$$\frac{Q_1 - Q_2}{Q_1} = \frac{\tau_1 - \tau_2}{\tau_1}. \quad \dots (7)$$

Since $(Q_1 - Q_2)$ represents the work W done by the reversible engine between the two temperatures τ_1 and τ_2, the new scale is called also the *work scale.*

The efficiency of the reversible engine on the thermodynamic scale is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\tau_2}{\tau_1}. \quad \dots (8)$$

In order that η may be equal to unity τ_2 should be zero. But the efficiency can be unity only when all the heat taken by the engine is converted into work, *i.e.*, when $Q_1 = W$ or $Q_2 = 0$ or $\tau_2 = 0$ This represents then *the zero of the thermodynamic scale.* A temperature less than $\tau_2 = 0$ is not possible, since then τ_2 will be negative which means that the efficiency η will be greater than one, which is impossible. In other words when τ_2 is less than zero Q_2 will be negative, which implies that the engine will be drawing heat from both the source and the sink, which is forbidden by the second law.

Having thus fixed the zero of the absolute scale, let us *determine the size of each degree* in it. Supposing that the reversible engine works between the boiling and freezing points of water at normal pressure, let ABCD represent the indicator diagram for the Carnot cycle of its operations (Fig 198). The work done by the engine is numerically given by the area ABCD. Let this area be divided into 100 equal parts. by isothermals drawn parallel to AB and CD. The area of each part will correspond to *one degree on the Kelvin's absolute scale,* which *may be defined as the difference in the temperatures between which the reversible engine should be worked to get energy equal to one-hundredth of the area of the indicator diagram representing Carnot's cycle between the temperatures of boiling water and melting ice.*

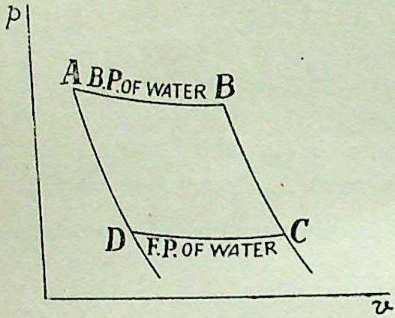


Fig. 198.

Keeping the temperature of the source constant at the boiling point of water, the work done by the engine will increase as the temperature of the sink is reduced. Supposing the adiabatic expansion BC to continue so that the working substance cools continuously, a stage would be eventually reached when the substance could expand no more. The isothermal corresponding to this stage is the zero isothermal, *i.e.*, the temperature of this isothermal is the zero degree of the absolute scale. According to the elementary kinetic theory, at that temperature all molecular motions cease and the molecules are set at rest, so that the substance is depleted of all its energy. But, more recent and refined theories indicate that at the absolute zero the substance is not devoid of all energy, but there is still an appreciable amount of energy left, which is known as the *zero point energy*. The explanation of such a rather startling discovery is beyond the scope of this book.

The problem of *how to realise in practice* the theoretically perfect absolute scale of temperature, that so successfully overcomes the fundamental difficulty of the arbitrary nature of the scales devised for the measurement of temperature, is next to be investigated. This problem also has been solved by showing that *the thermodynamic scale agrees completely with the perfect gas scale* as follows :—

We have already seen that for a reversible engine using a perfect gas as the working substance, the efficiency is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \qquad (Cf.\ \text{p. } 458) \qquad \ldots (9)$$

where T_1 and T_2 are the temperatures of the source and sink, measured on the perfect gas scale.

Comparing relation (9) with (8), we have

$$\frac{T_1}{T_2} = \frac{\tau_1}{\tau_2} \qquad \ldots (10)$$

This relation (10) indicates that the ratios of any two temperatures on the perfect gas scale and the thermodynamic scale are equal. Since, if $\tau_2 = 0$, T_2 is also $= 0$, the zero of the thermodynamic scale coincides with the zero of the perfect gas scale. If T_1 is the temperature of boiling water and T_2 that of melting ice, measured on the perfect gas scale

$$T_1 - T_2 = 100$$

On the thermodynamic scale we have for the same two fixed points, as shown above,

$$\tau_1 - \tau_2 = 100$$

Using the perfect gas scale, the efficiency

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{100}{T_1}$$

and in terms of the thermodynamic scale

$$\eta = \frac{\tau_1 - \tau_2}{\tau_1} = \frac{100}{\tau_1}$$

Since the efficiency is the same

$$\frac{100}{T_1} = \frac{100}{\tau_1}$$

This means that the temperatures of the boiling point of water and the melting point of ice are identical on the two scales. In a similar manner, it can be shown that any temperature has the same value on *the two scales*, which *are, therefore, identical.*

It may be noted that although the perfect gas scale cannot be realised directly, since actual gases only tend to the perfect gas at very low pressure, we have already indicated the method of reducing the scale of actual gas thermometers, such as the constant volume hydrogen thermometer, to the perfect gas scale. (*Cf*. pp. 36-38 and 99-100)

(*ii*) **Latent heat equation.** This equation, known as *Clausius-Clapeyron equation*, is of importance, as it throws light on the variation of the melting and boiling points of substances with pressure as well as on the specific heat of saturated vapour. Clapeyron deduced it in a rigorous manner by the application of the second law of thermodynamics, as follows :—

Let ABCD represent a complete isothermal covering the change of state at temperature T° K and EFGH a similar isothermal at temperature (T + dT)°K, dT being infinitely small. Along BC and FG, the change of state is in actual progress, the substance existing in both the phases (liquid and solid or vapour and liquid), while at B and C or at F and G, the substance exists in a single phase, at B all liquid, whereas at C all solid or at B all vapour and at C all liquid, similarly at G and F. From F and G let two adiabatics be drawn meeting the lower isothermal at I and J respectively. Let it be supposed that a unit mass of the substance is taken through a reversible Carnot cycle GFIJ, allowing it to expand isothermally along GF, adiabatically along FI, compressing it isothermally along IJ and adiabatically along JG. (Fig. 199).

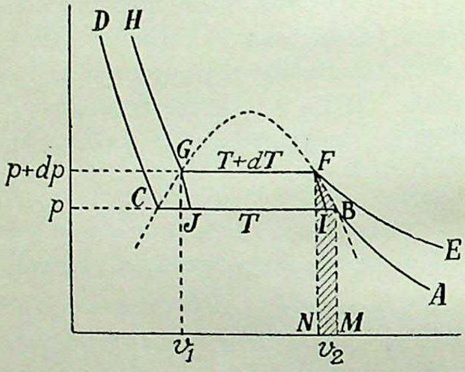


Fig. 199.

The amount of heat Q_1 absorbed along GF at T + dT is L + dL where L is the latent heat and the amount of heat Q_2 given up along IJ at T is L, since the latent heat varies with temperature.

Using the relation for the efficiency of a reversible cycle

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

and substituting the values of Q_1 and Q_2 and T_1 and T_2,

$$\frac{L + dL - L}{L + dL} = \frac{T + dT - T}{T + dT}$$

or $$\frac{dL}{L + dL} = \frac{dT}{T + dT}$$

or $$\frac{dL}{dT} = \frac{L + dL}{T + dT} = \frac{L}{T}$$

or $$dL = \frac{L}{T} \cdot dT \qquad \ldots (1)$$

The quantity of heat converted into work during the cycle

$$Q_1 - Q_2 = L + dL - L = dL \qquad \ldots (2)$$

The work done is also given by the area GFIJ = FG × perpendicular distance between GF and IJ in the limiting case

$$= dp\,(v_2 - v_1) \qquad \ldots (3)$$

where dp is the increase in pressure due to the increase in temperature by dT and v_1 and v_2 are the specific volumes of the substance at the states represented by G and F respectively.

$$\therefore \qquad dL = dp\,(v_2 - v_1),$$

dL being measured in work units.

Substituting for dL from (1)

$$\frac{L}{T} \cdot dT = dp\,(v_2 - v_1)$$

or $$\frac{dp}{dT} = \frac{L}{T\,(v_2 - v_1)} \qquad \ldots (4)$$

This relation (4) is known as the *Clapeyron latent heat equation.* It can be applied equally well to both the changes of state, *i.e.*, from solid to liquid and from liquid to vapour, since in our reasoning above we have assumed nothing which is not true of either change.

Application to the effect of pressure on the boiling and melting points :—

(*a*) *Effect of pressure on the boiling point*. Referring to Fig. 199, up to C the substance is wholly in the liquid state and along CB it exists partly in liquid and partly in the vapour state. The temperature T is, therefore, the boiling point of the liquid at a pressure corresponding to C, *i.e.*, p. Similarly up to G the substance is wholly in the liquid state and along GF partly liquid partly vapour. Hence the temperature T + dT is the boiling point corresponding to a pressure $p + dp$. At B the substance is wholly in the vapour state and similarly at F.

Since the specific volume of a substance is always much larger in the vapour state represented by F than in the liquid state represented by G, $(v_2 - v_1)$ is positive. Using this fact in relation (4), as L and T also are positive, $dp/d\mathrm{T}$ is positive. Hence *the boiling point of a liquid is raised with increase of pressure.*

Taking, for instance, water, the normal boiling point is 100°C and normal latent heat of vaporisation 540 calories. One gram of steam occupies a volume of 1677 c.c. Hence for an increase of one atmosphere, the elevation of the boiling point is given by

$$\frac{76 \times 13{\cdot}6 \times 980}{d\mathrm{T}} = \frac{540 \times 4{\cdot}2 \times 10^7}{373\ (1677 - 1)}$$

or

$$d\mathrm{T} = 27{\cdot}92^\circ\mathrm{C},$$

which agrees well with the value obtained in Holborn and Henning's experiments, *viz.*, 27·98°.

(*b*) *Effect of pressure on the melting point.* $(v_2 - v_1)$ is the change in volume which occurs when unit mass of the substance changes from the liquid to the solid state. *When a solid melts*, there may be *decrease in volume*, as in the case of *ice*, then $v_2 < v_1$ and $(v_2 - v_1)$ is negative. Since L and T are positive, $dp/d\mathrm{T}$ is negative. In such a case the *melting point decreases with increase of pressure. If the volume increases*, as in the case of *most substances*, $v_2 > v_1$ an $(v_2 - v_1)$ is positive, which means $dp/d\mathrm{T}$ is positive and *the melting point increases with pressure.*

In the case of ice, the normal melting point is 0°C and the latent heat of fusion = 80 calories ; $v_2 = 1$ c.c., $v_1 = 1{\cdot}091$ c.c. For an increase of pressure of 1 atmosphere, the depression of the freezing point is given by

$$\frac{76 \times 13{\cdot}6 \times 980}{d\mathrm{T}} = \frac{80 \times 4{\cdot}2 \times 10^7}{273\ (1 - 1{\cdot}091)}$$

or

$$\mathrm{T}d = -\ 0{\cdot}0074^\circ\mathrm{C},$$

which is in good agreement with Dewar's experimental value of $-\ 0{\cdot}0072^\circ$C.

Note : 1. When $v_2 = v_1$, relation (4) shows that either L = 0 or $dp/d\mathrm{T}$ is infinite. The former (*i.e.*, L = 0) is nearly verified in the case of vaporisation at a temperature approaching the critical point, while the latter (*i.e.*, $dp/d\mathrm{T} = \infty$) is realised to some extent in the case of fusion where $v_2 - v_1$ is very small and $dp/d\mathrm{T}$ very large.

2. *Internal and external latent heats.* When a change of state occurs with change of volume, the heat necessary for the transfor-

mation, *viz* , the latent heat L, is the sum of two parts, one part, known as the *internal latent heat* (L_i) and sometimes called the "true latent heat" which is spent in altering the internal energy of the substance, and the other, known as the *external latent heat* (L_e) which is spent in doing external work due to the change of volume, as already indicated. (*Cf.* p. 197).

$$\therefore \qquad L = L_i + L_e$$

We have already shown that

$$L_e = p\,(v_2 - v_1) \qquad (Cf.\ \text{p. } 383)$$

$$\therefore \qquad L_i = L - p\,(v_2 - v_1)$$

$$\text{But} \qquad L = T\,(v_2 - v_1)\,\frac{dp}{dT} \quad \text{[from relation (4)]}$$

$$\therefore \qquad L_i = T\,(v_2 - v_1)\,\frac{dp}{dT} - p\,(v_2 - v_1)$$

$$= T\,(v_2 - v_1)\left\{\frac{dp}{dT} - \frac{p}{T}\right\}$$

$$= T^2\,(v_2 - v_1)\,\frac{d}{dT}\left(\frac{p}{T}\right)$$

This relation offers a means of estimating the internal latent heat.

(*iii*) **Specific heat of saturated vapour.** Clausius obtained the latent heat equation in a different form, by means of which the specific heat of saturated vapour can be studied. We have already indicated that the specific heat of a saturated vapour can be neither C_p nor C_v and can be either positive or negative (*Cf.* p. 166). We are now going to study this problem with the help of the second law of thermodnamics using the Clausius' latent heat equation, which may be derived as follows :—

Let s_1 denote the specific heat of a liquid in contact with its vapour and s_2 the specific heat of the saturated vapour in contact with its liquid.

Considering the cycle CGFB (Fig. 199), the amount of *heat absorbed* by the substance (liquid) during its passage from C to G when the temperature rises by dT

$$= s_1\,dT$$

and the amount of *heat absorbed* along GF when the substance changes from liquid into vapour

$$= L + dL$$

The amount of *heat given back* by the substance (vapour) along the path FB when its temperature falls by dT

$$= s_2\, dT$$

and the amount of *heat given up* by the substance along BC when it condenses into liquid

$$= L$$

∴ The net amount of heat used during the cycle is

$$s_1 dT + L + dL - s_2 dT - L = (s_1 - s_2)\, dT + dL$$

This must be equal to the work done which is given by the area GFIJ in the limiting case and hence

$$= dp\,(v_2 - v_1) = \frac{L}{T} \,.\, dT$$

as proved in the previous section.

$$\therefore \quad (s_1 - s_2)\, dT + dL = \frac{L}{T} .\, dT$$

$$\therefore \quad s_2 - s_1 = \frac{dL}{dT} - \frac{L}{T} \qquad \dots (5)$$

This relation (5) is known as *the latent heat equation of Clausius* and it enables the specific heat of saturated vapour to be calculated.

At the point F the substance is in the saturated vapour state at a temperature $T + dT$ and at B it is still in the saturated vapour state but at a temperature T. The dotted curve joining B and F is the *saturation curve.*

Although s_1 is neither C_p nor C_v strictly speaking, yet s_1 does not appreciably differ from C_p, as the effect of pressure is too small to bring about any considerable change in the state of the liquid ; hence s_1 can be put equal to C_p and the value of s_2, the specific heat of saturated vapour can be calculated.

For water, at 100°C = 373°K, $L = 539$ calories, $dL/dT = -\,0{\cdot}64$ calories as obtained from Regnault's experiments, $s_1 \approx C_p = 1{\cdot}01$. Substituting these values in relation (5)

$$\begin{aligned} s_2 &= 1{\cdot}01 - 0{\cdot}64 - \frac{539}{37} \\ &= 1{\cdot}01 - 0{\cdot}64 - 1{\cdot}44 \\ &= 1{\cdot}01 - 2{\cdot}08 = -\,1{\cdot}07. \end{aligned}$$

Thus the specific heat of saturated water vapour at 100°C turns out to be a *negative* quantity. This rather paradoxical result can be explained on the basis that the *condition of saturation of the vapour has to be always satisfied.*

In order, therefore, to keep the vapour saturated throughout its passage from F to B, (Fig. 199) the pressure and volume have to be adjusted in such a manner that it keeps to the saturation curve FB. In passing from B to F the volume decreases and the pressure increases, so that external work is done on the vapour, which is given by the shaded area FBMN. This work done on the vapour appears as heat Let this quantity of heat be equal to H_1 when the temperature rises by 1°C, *i.e.*, when $dT = 1°C$. Let H_2 be the quantity of heat supplied from outside to the vapour to raise its temperature through 1°C. In this process the vapour expands and becomes unsaturated. In order to keep it saturated it has to be compressed and hence the quantity of heat H_1 which is produced due to compression, will have to be removed from the system if the vapour has to remain saturated. Now three cases arise :—

(*i*) When $H_2 = H_1$ In this case the net quantity of heat absorbed by the vapour is zero, so that *the specific heat of the saturated vapour is zero*

(*ii*) When $H_2 > H_1$. The net quantity of heat absorbed by the vapour is positive. In such a case, *specific heat of saturated vapour is positive.* In other words, to raise the temperature of the vapour keeping the vapour saturated, heat has to be supplied from outside.

(*iii*) When $H_2 < H_1$. The net quantity absorbed by the vapour $(H_2 - H_1)$ is negative. In such a case *the specific heat of the saturated vapour is negative.* In other words, heat has to be removed from the vapour in order to raise its temperature, while keeping it saturated

Note : For the same saturated vapour when the temperature is varied, the specific heat will vary from − ve to + ve. For, taking the expression

$$s_2 = s_1 + \frac{dL}{dT} - \frac{L}{T}$$

Since $\frac{dL}{dT}$ is invariably negative, $\left(\frac{dL}{dT} - \frac{L}{T}\right)$ is always negative. For low values of T, $\left(\frac{dL}{dT} - \frac{L}{T}\right)$ is numerically greater than s_1 ; hence s_2 may be − ve. As temperature increases $\frac{L}{T}$ diminishes and $\left(\frac{dL}{dT} - \frac{L}{T}\right)$ decreases, so that at a certain stage it may be equal to s_1 ; then s_2 is zero. For higher temperatures s_2 is + ve. The temperature at which specific heat passes from the negative to the positive values is called the *temperature of specific heat inversion.*

At the critical temperature, since $L = 0$, and $dL/dT = -\infty$, $s_2 = -\infty$; thus the specific heat of every saturated vapour becomes — ve and increases indefinitely in numerical value as the critical temperature is approached. If all substances behave in this way, *i.e.*, $s_2 = -\infty$ at the critical temperature, since in all known cases s_2 increases with rise of temperature, any substance must pass through a maximum value at some temperature below the critical temperature. Consequently, if there be a point of inversion at ordinary temperature at which s_2 passes from — ve to + ve value, there must also be a second point of inversion below the critical temperature at which it changes from + ve to — ve value. Thus there may be *two points of inversion*, but if only one, it must be the latter, *i.e.*, below the critical temperature.

(*iv*) **Refrigeration.** In Chapter VII we have described refrigerating machines and considered the general principles upon which they work. We shall now investigate the problem of refrigeration as an application of the second law of thermodynamics. A refrigerator is essentially a heat engine worked backwards. It has all the essentials of such an engine, but only it absorbs heat from the cold body and transfers it to the hot body. According to the second law of thermodynamics, heat cannot be transferred from a cold to a hot body without expenditure of work and the refrigerating machine is precisely designed to do that work.

The efficiency of different refrigerating machines can be compared by a quantity called the *coefficient of performance*, which is defined as *the ratio of the heat abstracted from the cold body to the work done by the machine*. Assuming that the machine performs the Carnot cycle in the reverse direction, if Q_2 is the quantity of heat abstracted from the cold body at a temperature T_2 and Q_1 the quantity of heat given up to the hot body at a temperature T_1 the work done by the machine is $Q_1 - Q_2$. Hence the coefficient of performance of an ideal refrigerating machine is given by

$$\frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

It can be shown, as in the case of the reversible heat engine that *all perfectly reversible refrigerating machines working between the same* *two temperatures have the same coefficient of performance.* Hence the coefficient of performance of any perfectly reversible refrigerating machine working between temperatures T_1 and T_2 is equal to $T_2/(T_1 - T_2)$ which is the maximum possible, whatever be the nature of the working substance. The most efficient arrangement for a refrigerating machine working at a given lower temperature T_2 is that for which $T_1 - T_2$ is as small as possible.

A Carnot engine using perfect gas and working backwards will be the most efficient refrigerating machine, but its output will be small due to the small thermal capacity of gases. For large output, a liquid of large latent heat of vaporisation is to be employed and allowed to evaporate at the lower temperature. We have already seen that ammonia, sulphur dioxide, freon, etc., are best suited for this purpose.

The efficiency of an actual refrigerator such as the vapour compression machine described on p. 438 may be calculated as follows. The cycle of operations which the working substance undergoes may be represented on indicator diagram, as shown in Fig. 200. AB represents the evaporation of the liquid in the cold storage space, BC the adiabatic compression of the vapour by the compressor, CD the liquefaction of the substance in the condenser and DA the adiabatic expansion of the liquid. The cycle ABCD is perfectly reversible and hence its coefficient of performance is given by $T_2/(T_1 - T_2)$.

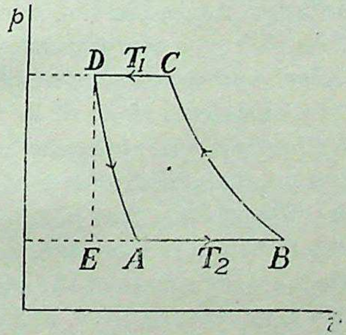


Fig. 200.

In the actual machine the regulating valve takes the place of the expansion chamber, for the sake of mechanical simplicity. In consequence the part DA of the ideal cycle is to be replaced by DEA. On account of the irreversible expansion through the valve there is a loss of efficiency in two ways, *viz.*, an amount of work equal to the area DEA is lost and a reduced refrigeration effect is produced, as some liquid evaporates before reaching the cold storage space.

(*v*) **Radiation in a uniform temperature enclosure.** In Chapter V, in connection with *black body radiation*, we have stated that the quantity and quality of the radiation in a uniform temperature enclosure depend only on its temperature and are entirely independent both of the nature of the walls and of any substance which may be inside it. We shall now prove this statement by the application of the second law of thermodynamics.

Let us suppose that we have two enclosures A and B, having walls of different shape and material, but maintained at the same temperature. Let A and B communicate with each other by means of a tube which is normally closed by a plate impervious to all radiation. *Let us suppose that the energy density of radiation in A is greater than that in B, if possible.* If now the plate which cuts off all communication between A and B is removed for a certain time some radiation will pass from A to B. Let the plate be replaced and A and B allowed to arrive at equilibrium with their radiation once more. The excess radiation received by B will be absorbed by its walls and raise its temperature, while the temperature of the walls of A will fall on account of the loss of radiation from it. The difference of temperature between B and A thus produced can be made to work a Carnot engine yielding a certain amount of work, which has been derived from a source of heat originally all at one temperature. In other words, we have created a temperature difference between the two enclosures A and B without expenditure of work. This is evidently contrary to the second law of thermodynamics. Hence the original assumption that the energy density of radiation in A is different from that in B is incorrect, and so the energy density of the radiation in a uniform temperature enclosure is entirely independent on the nature of the walls of the enclosure and depends only on the temperature.

What we have proved for radiation as a whole can also be shown to be true for each infinitesimal band of wavelengths into which the radiation can be divided by merely replacing the plate by a screen which allows only the band of wavelengths under test for a certain time. Likewise, introducing some material body in one of the enclosures it can be shown, by a similar reasoning, that the radiation in the enclosure is unaffected by the presence of the body. Hence both the quantity and quality of radiation inside a uniform temperature enclosure depend solely on the temperature, independent of the nature of the walls or the presence of other bodies in the enclosure, if the second law of thermodynamics is to be maintained.

ENTROPY

Introduction. In the formulation and application of the second law of thermodynamics, Clausius was the first to introduce a new physical quantity, called entropy, which has proved to be of great importance not only in the further development of thermodynamics but also in the recognition of a fundamental law of Nature. Having realised that the problem of continuous conversion of heat into work, with which the second law deals, was largely dependent on the *direction* rather than the actual amount of energy change in a system, he found that the new concept, entropy, could cover adequately that additional factor. He saw also that, in the application of the second law, the change of the thermal state of the working substance was much more important than the general idea of mere convertibility of heat into work, since it was the working substance alone which underwent a thermodynamical change in the process, and found that entropy could efficiently define the thermodynamical state of any working substance. Another reason, which induced him to have recourse to the new concept of entropy, was to have a physical property of a substance that could remain constant in adiabatic changes, like temperature in isothermal changes.

These arguments, which convinced Clausius that the second law should be restated in terms of entropy, will be made clear as we proceed with the study of the definition and characteristics of entropy.

General notions about entropy. Considering a number of isothermals at temperatures T_1, T_2, T_3...etc. on a p-v diagram let A and B be two adiabatics which cut the isothermals at a and b, c and d, e and f...... (Fig. 201). Let $abdc$ and $cdfe$ represent ideal Carnot cycles. Taking the cycle $abdc$, if Q_1 be the heat absorbed at T_1 and Q_2 the heat given out at T_2, then by Carnot's principle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}.$$

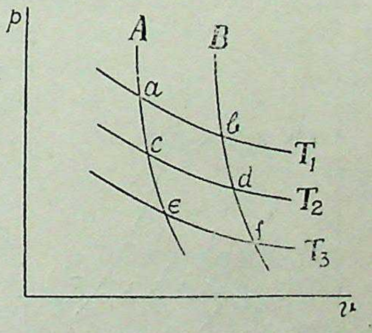


Fig. 201

Considering the cycle $cdfe$, if Q_2 is the heat absorbed at T_2 and Q_3 the heat liberated at T_3,

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}.$$

Similar relations are obtained for other cycles formed by the crossing of the two adiabatics with other isothermals.

$$\therefore \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} \ldots = \text{constant}$$

Hence, in general, if Q is the quantity of heat absorbed or liberated at a temperature T in going from one adiabatic to the other, then

$$\frac{Q}{T} = \text{constant } (\varphi)$$

This constant ratio is known as the **change of entropy** between the states represented by the two adiabatics.

If the adiabatics under consideration lie very close together and dQ is the quantity of heat absorbed or liberated at the temperature T ; the small change in entropy $d\varphi$ is given by

$$d\varphi = \frac{dQ}{T}.$$

Hence the change of entropy $\varphi_2 - \varphi_1$ in passing from an adiabatic A to another B is given by

$$\varphi_2 - \varphi_1 = \int_A^B \frac{dQ}{T}.$$

Considering any one of the adiabatics, since no heat enters or leaves a system in adiabatic changes, $dQ = 0$, so that $dQ/T = 0$. This means that there can be *no change of entropy in an adiabatic change*, or **the entropy remains constant in adiabatic changes.** Hence the adiabatic curves on the *p-v* diagram are called *isentropics, i.e.*, curves of constant entropy.

Change of entropy is independent of path. We have seen above that the change of entropy between two adiabatics is constant, whatever be the isothermal path chosen for traversing from one to the other. We shall now proceed to show that the same conclusion holds whatever be the nature of the path chosen to go from the adiabatic A to the adiabatic B, be it isothermal or even adiabatic or both. Let A and B be the two adiabatics representing two states. Let CD represent any reversible transformation which takes the working substance from the state A to the state B at a temperature T. The whole transformation CD may be considered as being made up of a large number of very

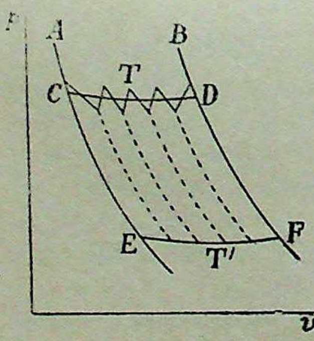


Fig. 202.

small transformations, which are alternately isothermal and adiabatic, represented by the zig-zag curve super-imposed on CD, the successive elements of which are alternately elements of isothermal and adiabatic curves. Considering an isothermal EF at some temperature T′ between the two adiabatics A and B, let the elementary adiabatics on CD be prolonged up to the isothermal EF as shown in Fig. 202.

Each small element thus formed represents a small Carnot cycle, so that we have

$$\frac{dQ}{T} = \frac{dQ'}{T'}.$$

In the limit when the Carnot cycles are infinitely small, the zig-zig curve coincides with CD, and hence,

$$\int_A^B \frac{Q}{T} = \int \frac{dQ'}{T}.$$

But the quantity $\int \frac{dQ'}{T'}$ which represents the change of entropy along the isothermal EF is a constant, wherever this isothermal is drawn.

$$\therefore \qquad \int_A^B \frac{dQ}{T} \text{ is a constant}$$

irrespective of the actual path of the curve between A and B. Hence the change of entropy depends only on the states of a system at the start and end of the change and is quite independent of the way in which the change is made.

Entropy of state. For calculating the entropy of a system at any of the two states, a state of zero entropy will have to be considered, as in the case of other quantities, such as height and potential, an arbitrary zero is chosen. Thus, in the present case

$$\therefore \qquad \int_0^A \frac{dQ}{T} = \varphi_1 \text{ and} \int_0^B \frac{dQ}{T} = \varphi_2.$$

Hence to measure the entropy of any state the working substance has to be taken along any reversible process to its zero state and the value of $\int_0^T \frac{dQ}{T}$ along this process has to be found. In this way, evidently, the absolute value of the entropy of the state cannot be found, since the zero state is chosen arbitrarily. In dealing with actual problems where only changes of entropy are involved, the measurement of entropy of a single state is not necessary. But the idea of the entropy of a single state helps to define the *entropy of a substance* as we shall see presently, so that Clausius identified the two.

Change of entropy in reversible processes. In a reversible cycle there are two adiabatic and two isothermal processes. During the adiabatic processes there is no absorption or liberation of heat and hence no change in entropy. Of the two isothermal processes, one is an expansion, in which an amount of heat Q_1 is absorbed at a temperature T_1 and the other a compression, in which another amount of heat Q_2 is liberated at a temperature T_2. In the former there is gain of entropy of $\frac{Q_1}{T_1}$, while in the latter a loss of entropy of $\frac{Q_2}{T_2}$. Hence the net change in entropy for the whole cycle $= \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$.

But since for a reversible cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

the *net change in entropy is zero*. In other words, *the entropy of a system remains constant in all reversible processes.*

Change of entropy in irreversible processes. Taking the simple case of *conduction or radiation of heat* which are irreversible processess, let a system consist of two bodies at temperature T_1 and T_2, $T_1 > T_2$. As heat will always travel from the hotter to the colder body by conduction or radiation, if Q is the quantity of heat thus transmitted,

$$\text{loss of entropy by the hot body} = \frac{Q}{T_1}$$

$$\text{gain of entropy by the cold body} = \frac{Q}{T_2}$$

$\therefore$ Net gain in entropy of the system $= Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ which is positive, since $T_1 > T_2$.

Considering another irreversible process such as the *free expansion of a gas into vacuum*, one arrives at the same conclusion. For the sake of simplicity, let us suppose that a perfect gas in a vessel rushes into an evacuated vessel, the whole system being isolated. Since the gas is perfect the temperature does not change in the process. During the isothermal expansion of the gas against a pressure which is always just less than the pressure of the gas, the work done by the gas for a small change dv in volume is pdv. The corresponding change of entropy

$$d\varphi = \frac{dQ}{T} = \frac{pdv}{T} = R\frac{dv}{v}.$$

$\therefore$ The change of entropy when the gas expands from a volume v_1 to volume v_2 is given by $\varphi = \int_{v_1}^{v_2} R \frac{dv}{v} = R \log_e \frac{v_2}{v_1}$. Since $v_2 > v_1$ and R is a positive quantity, φ is always positive and hence the entropy of the system increases.

In general, therefore, *the entropy of a system increases in all irreversible processes* which is known as the **law of increase of entropy,** a law of great importance, as we shall see presently.

Entropy and unavailable energy. In a Carnot cycle a quantity of heat Q_1 is absorbed from the source at a temperature T_1 and a quantity of heat Q_2 is given up to the sink at a lower temperature T_2 so that only $(Q_1 - Q_2)$ is available for useful work, while Q_2 is the unavailable portion of the energy. Using Carnot's principle, *viz.,* $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$, the unavailable energy Q_2 is given by

$$Q_2 = \frac{Q_1}{T_1} \cdot T_2$$

Hence for a given sink, *i.e.,* for a given value of T_2, the unavailable energy is determined by the increase in entropy during the isothermal process at T_1. Thus *entropy is a measure of the unavailability of energy in a system, i.e.,* the greater the increase in entropy of a system, the smaller the energy available for useful work from it. This result shows *the law of increase of entropy must be intimately connected with the law of degradation or dissipation of energy,* again a very important conclusion, with which we shall deal at length below.

With these general notions about entropy, we can now proceed to define entropy and formulate the second law in terms of entropy.

Definition of entropy. Entropy is *that thermal property of a substance which remains constant when the substance undergoes adiabatic changes,* where no heat is communicated to it or taken away from it by the surroundings. It is a physical quantity, although there is nothing physical to represent it and it cannot be felt like temperature or pressure. Although the idea of entropy is necessitated by the existence of irreversible processes, it is a definite single-valued function of the thermodynamical coordinates defining the state of the substance, *viz.*, the temperature, pressure, volume or internal energy.

Entropy, though conveniently measured in terms of a reversible process, has nothing to do with it and exists quite independently of it. For, the first law of thermodynamics states that

$$dQ = du + pdv$$

for any process reversible or irreversible, provided the work done by the substance is by expansion against an external pressure p.

Now, to find the entropy of the substance, we have to get the value of dQ along a reversible process. The process is reversible when the external pressure p is always equal to the intrinsic pressure of the substance, *i.e.*, when the expansion is balanced. Hence, considering unit mass of the substance, we have

$$\varphi = \int \frac{dQ}{T} = \int \frac{du + pdv}{T},$$

where p now represents the intrinsic pressure of the substance.

It is readily seen that *entropy is proportional to the mass of the substance*. For, if we take m gms. of the substance,

$$dU = m \,.\, du, \quad dV = mdv,$$

so that the entropy of the substance is given by

$$m\,\varphi$$

where φ is the entropy per unit mass.

The entropy of a substance is measured in calories per degree or ergs per degree. A substance is said to have zero entropy when it is at 0°C and 760 mm. pressure, arbitrarily chosen.

Similarly the *entropy of a system* consisting of bodies in thermodynamic equilibrium and having masses m_1, m_2...etc., and specific entropies φ_1, φ_2...etc., is given by

$$m_1\varphi_1 + m_2\varphi_2 + \ldots$$

Thus it appears that entropy is a real physical quantity, though intangible and not directly representable by anything that can be visualised.

It may be noted that entropy, when applied to a system made up of a large number of bodies, is *a statistical property closely connec-*

ted with the probable state of the system, increase of entropy implying a transition from a less probable to a more probable state. This interesting aspect of entropy is of far reaching importance and will be dealt with below.

In order to realise that entropy is a real physical quantity, we shall calculate the entropy in some particular cases.

Entropy of a perfect gas. Consider one gram of a perfect gas at a pressure p and temperature T occupying a volume v. If dQ is the amount of heat given to the gas, its *entropy* φ is given by the relation

$$\varphi = \int \frac{dQ}{T} = \int_0^T \frac{du + pdv}{T} \qquad \dots (1)$$

But $du = C_v \, . \, dT$, where C_v is the specific heat at constant volume,

and $$p = \frac{RT}{v},$$

where R is the gas constant.

$$\therefore \qquad \varphi = \int_0^T C_v \frac{dT}{T} + R \frac{dv}{v}$$
$$= C_v \log_e T + R \log_e v + \text{constant}$$
$$= C_v \log_e T + (C_p - C_v) \log_e v + \text{constant} \dots (2)$$

since $R = C_p - C_v$, where C_p is the specific heat at constant pressure.

The entropy φ can be expressed also in terms of pressure.

Since $pv = RT, \; v = \dfrac{RT}{p}$

and $$pdv + vdp = RdT$$

$$\varphi = \int_0^T C_v \frac{dT}{T} + \frac{(RdT - vdp)}{T}$$
$$= \int_0^T C_v \frac{dT}{T} + R\left(\frac{dT}{T} - \frac{dp}{p}\right)$$

Substituting for $R = C_p - C_v$,

$$\varphi = \int_0^T C_v \frac{dT}{T} + (C_p - C_v)\left(\frac{dT}{T} - \frac{dp}{p}\right)$$
$$= \int_0^T C_p \frac{dT}{} - (C_p - C_v) \frac{dp}{p}$$
$$= C_p \log_e T - (C_p - C_v) \log_e p + \text{constant} \dots (3)$$

Similarly the entropy can be expressed in terms of pressure and volume by eliminating T, as follows :—

$$\text{As} \qquad T = \frac{pv}{R} \text{ and } dT = \frac{pdv + vdp}{R}$$

$$\varphi = \int_0^T C_v \frac{pdv + vdp}{RT} + \frac{pdv}{T}$$

$$= \int_0^T C_v \frac{pdv + vdp}{pv} + \frac{pdv\,R}{pv}$$

$$= \int_0^T C_v \left(\frac{dv}{v} + \frac{dp}{p}\right) + (C_p - C_v)\frac{dv}{v}$$

$$= \int_0^T C_v \frac{dp}{p} + C_p \frac{dv}{v}$$

$$= C_v \log_e p + C_p \log_e v + \text{constant} \qquad \ldots (4)$$

The *change of entropy* $(\varphi_2 - \varphi_1)$ when the gas changes from a state of pressure p_1, volume v_1 and temperature T_1 to another of p_2, v_2 and T_2 is obtained readily by integrating relation (1) between limits T_1 and T_2 instead of between 0 and T. Thus, relations (2), (3) and (4) become

$$\varphi_2 - \varphi_1 = C_v \log_e \frac{T_2}{T_1} + (C_p - C_v)\log_e \frac{v_2}{v_1} \qquad \ldots (5)$$

$$= C_p \log_e \frac{T_2}{T_1} - (C_p - C_v)\log_e \frac{p_2}{p_1} \qquad \ldots (6)$$

$$= C_v \log_e \frac{p_2}{p_1} + C_p \log_e \frac{v_2}{v_1} \qquad \ldots (7)$$

Any one of the three expressions (5), (6) and (7) can be used to calculate the change of entropy.

The *change of entropy for m gms. of the gas*, is got by multiplying $(\varphi_2 - \varphi_1)$ by m, *i.e.*, by multiplying relation (5), (6) or (7) by m.

Entropy of steam. Let us find an expression for the gain in entropy when 1 gram of ice at T_1°K changes into steam at T_2°K. Let L_1 and L_2 be the latent heats of the ice and steam respetively. The total change in entropy can be calculated as follows :—

The change in entropy is given by the relation $d\varphi = \dfrac{dQ}{T}$.

When 1 gm. of ice at T_1°K changes into water without any change in temperature, the change in entropy $= \dfrac{L_1}{T_1}$.

When 1 gm. of water at T_1°K is heated to T_2°K, the change in entropy

$$= \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{s\,dT}{T}$$

$$= s \log_e \frac{T_2}{T_1}$$

where s is the specific heat of water, assumed constant.

When 1 gm. of water at T_2°K changes into steam at the same temperature, the change in entropy $= \frac{L_2}{T_2}$.

∴ The total gain in entropy

$$= \frac{L_1}{T_1} + s\log_e \frac{T_2}{T_1} + \frac{L_2}{T_2}$$

Let us use this relation in one or two *numerical examples* :–

(1) Find the increase in entropy when 1 gm. of ice at 0°C changes into 1 gm. of steam at 100°C, assuming the specific heat of water as 1, latent heat of ice = 80 cals./gm. and latent heat of steam = 540 cals./gm.

The increase in entropy

$$= \frac{80}{273} + 2\cdot3026 \log_{10} \frac{373}{273} + \frac{540}{373}$$

$$= 0\cdot293 + 0\cdot312 + 1\cdot448$$

$$= 2\cdot053 \text{ cals. per degree.}$$

(2) Find the increase in entropy when 20 gms. of ice at 0°C melts into water at the same temperature, given L = 80 cals./gm.

Increase in entropy $= \frac{80 \times 20}{273} = 5\cdot86$ cals./°C.

(3) Find the change in entropy when 1 gm. of water boils under a pressure of 174·39 cms.

The boiling point of water under the given pressure, as given in tables = 125°C and the latent heat of steam at this temperature = 518·7 cals./gm.

∴ Change in entropy $= \frac{518\cdot7}{273+12} = 1\cdot303$ cals./°C.

Temperature-entropy diagram. The thermodynamic state of a substance can be determined by plotting the temperature against entropy. The graph thus obtained is known as the *temperature-*

entropy diagram. Let us study a Carnot cycle represented by a *p-v* diagram and a T — φ diagram.

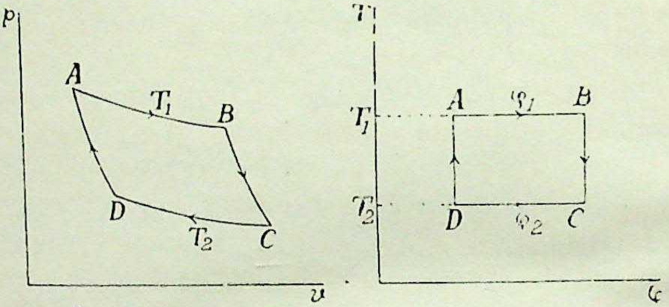


Fig. 203.

In the T — φ diagram, the isothermal AB at T_1°K runs parallel to the X-axis and the gain in entropy $= \frac{Q_1}{T_1}$. Along the adiabatic BC, running parallel to the Y-axis, there is no change in entropy, but a fall of temperature $T_1 - T_2$. CD is the second isothermal involving an equal loss in entropy $= \frac{Q_2}{T_2}$ and DA the second adiabatic involving an equal rise of temperature.

While the area ABCD in the *p-v* diagram gives the useful work obtained during a cycle, the area ABCD in the T — φ diagram represents the actual amount of energy converted into work.

The area ABCD in the T — φ diagram

$$= \varphi_1 (T_1 - T_2) = \varphi_2 (T_1 - T_2)$$

Since $\varphi_1 = \frac{Q_1}{T_1}$ and $\varphi_2 = \frac{Q_2}{T_2}$

and $\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q}{T_1 - T_2}$

area of ABCD $= \frac{Q_1 - Q_2}{T_1 - T_2} (T_1 - T_2) = Q_1 - Q_2$

∴ ABCD represents the energy converted into work.

The efficiency is given by

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{(T_1 - T_2)\, \varphi_1}{T_1 \varphi_1} = \frac{T_1 - T_2}{T_1}$$

a result which has already been obtained.

The T — φ graph, known as *tephigram* is extensively used in meteorology. It may be noted that the T — φ diagram of a cycle is of importance in the checking of the efficient working of actual engines. Any deviation in the T — φ diagram, indicating a change in entropy during a cycle, shows at once that the amount of energy available for useful work is on the decrease due to some irreversible processes having crept in and thus gives a timely warning against a possible breakdown of the engine.

T — φ diagram from one gram of water at 0°C being converted into steam. As it is usual to put the entropy of water at 0°C or 273°K equal to zero, O will represent the starting point of T — φ graph. (Fig. 204). The change in entropy when water at 0°C is heated to 100°C is given by

$$s \log_e \frac{373}{273}$$

where s is the specific heat of water = 1. This is represented by the logarithmic curve OA. The change in entropy when water 100°C is converted into dry steam at the same temperature is given by $\frac{L}{T}$ where L is the latent heat of steam and T = 373°K, assuming that the water boils under normal pressure. AB represents the increase in entropy during the change of state. If the steam is superheated to T′°K the entropy is further increased by the amount $s' \log_e \frac{T'}{T}$ where s' is the specific heat of steam during superheating, As s' varies with temperature, the average value over small intervals is taken. The change in entropy during this process is represented by the logarithmic curve BC. The curve OABC is the T — φ diagram of the process studied and the area OABCD represents the amount of thermal energy absorbed by water when it passes from 0°C to a superheated steam state.

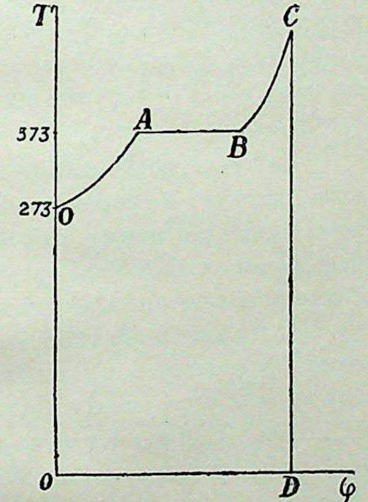


Fig. 204.

Law of increase of entropy. We have seen that the entropy increases in irreversible processes, while it is constant in reversible processes. These experimental facts have been generalised into the law of increase of entropy, which may be stated thus : *the entropy of an isolated system either remains constant or increases according as the changes it undergoes are reversible or irreversible.* Analytically expressed, $d\varphi \geqslant 0$, according as the change is irreversible or reversible. Hence the necessary and sufficient condition of equilibrium of an isolated system is that its entropy should be maximum, for then φ cannot increase and $d\varphi$ cannot be greater than zero. When this condition is reached no further change can occur and no further transformation of energy is possible.

We have also seen that the increase of entropy measures the non-availability of useful energy. Since energy is only available in a useful form as long as there are supplies of heat at different temperatures, it follows that the state of maximum entropy corresponds to that where all temperature differences are equalised.

In the physical universe, as long as differences of temperature exist, irreversible processes, like conduction, radiation, etc., will take place and the entroy will go on increasing with the consequent decrease of available energy. But when the universe reaches a stage where all its heat is at the same temperature its entropy would have reached its maximum value and the heat of the universe can no more be converted into useful work. This state is inevitably being approached since many factors are at work equalising temperature difference. This is referred to as *degradation of energy*, which implies that although the total amount of energy is conserved, energy is assuming a form which makes it less useful. It looks as if the universe is marching along towards a "*heat-death*."

The law of increase of entropy is intimately linked also with the less ordered state of affairs, growth of entropy implying a transition from order to disorder. According to this, a high entropy system should be in great disorder or chaos, as illustrated by a gas in which the molecules move about in great disorder filling the whole available space. When the gas is condensed into the liquid state, the molecules get more orderly and the entropy is lowered. When the liquid solidifies, the molecules get arranged in great order with a still further decrease of entropy, so that a crystal would represent a low entropy system. Hence as the temperature of a system is lowered the amount of disorder in it decreases. Hence the 'heat-death' of the material universe refers to a *state of stagnation* resulting from equalisation of all temperature differences with the consequent minimum useful energy available, maximum entropy and the greatest disorder due to the disappearance of all dissymmetry among the parts.

Formulation of the second law in terms of entropy can now be made as follows : *Every physical or chemical process in nature takes place in such a manner that the total entropy increases.* This is the most general statement of the second law and is identical with the law of increase of entropy or the law of degradation of energy.

Clausius summed up the *first law* by saying that the *energy of the universe remains constant* (the law of conservation of energy) and the *second law* by saying the *entropy of the universe tends to a maximum* (the law of increase of entropy or the law of degradation of energy or the law of increase of disorder).

THERMODYNAMICAL RELATIONS

Maxwell, making use of the two laws of thermodynamics in a convenient form, was ab e to derive a set of fundamental relations, known as *thermodynamical relations*, which find ready application to particular problems. We shall, therefore, deduce these relations and indicate their application to some thermal phenomena.

In general, the condition of a substance is completely determined by any pair of the quantities, p, v, T and φ. In solving, therefore, any thermodynamic problem, the pair most suitable is chosen as independent variables.

The first law of thermodynamics can be mathematically expressed as

$$dQ = dU + pdv$$

or

$$dU = dQ - pdv$$

The second law of thermodynamics can be similarly expressed as

$$dQ = Td\varphi$$

Combining the two, we get the fundamental thermodynamic formula

$$dU = Td\varphi - pdv \qquad \dots (1)$$

Let us express this relation in terms of two independent variables x and y, that will determine the condition of the substance (x and y may be any two of the quantities p, v, T and φ, which will be fixed later).

Since φ and v are supposed to be expressible in terms of x and y,

$$d\varphi = \left(\frac{d\varphi}{dx}\right)_y dx + \left(\frac{d\varphi}{dy}\right)_x dy$$

$$dv = \left(\frac{dv}{dx}\right)_y dx + \left(\frac{dv}{dy}\right)_x dy$$

$$\therefore\ dU = T\left(\frac{d\varphi}{dx}\right)_y dx + T\left(\frac{d\varphi}{dy}\right)_x dy - p\left(\frac{dv}{dx}\right)_y dx - p\left(\frac{dv}{dy}\right)_x dy$$

$$= \left[T\left(\frac{d\varphi}{dx}\right)_y - p\left(\frac{dv}{dx}\right)_y\right] dx + \left[T\left(\frac{d\varphi}{dy}\right)_x - p\left(\frac{dv}{dy}\right)_x\right] dy$$

$$\therefore\quad \left(\frac{dU}{dx}\right)_y = T\left(\frac{d\varphi}{dx}\right)_y - p\left(\frac{dv}{dx}\right)_y$$

and $$\left(\frac{dU}{dy}\right)_t = T\left(\frac{d\varphi}{dy}\right)_x - p\left(\frac{dv}{dy}\right)_x$$

The change in the internal energy dU, broght about by changing v and T, is the same whether we first make the change dv in v and then the change dT in T or the other way about. Mathematically this means that dU is a *perfect differential* and hence

$$\frac{d}{dy}\left(\frac{dU}{dx}\right)_y = \frac{d}{dx}\left(\frac{dU}{dy}\right)_x$$

i.e., $$\frac{d}{dy}\left[T\left(\frac{d\varphi}{dx}\right)_y - p\left(\frac{dv}{dx}\right)_y\right] = \frac{d}{dx}\left[T\left(\frac{d\varphi}{dy}\right)_x - p\left(\frac{dv}{dy}\right)_x\right]$$

$$\therefore\quad \left(\frac{dT}{dy}\right)_x\left(\frac{d\varphi}{dx}\right)_y + T\,\frac{d^2\varphi}{dy\,.\,dx} - \left(\frac{dp}{dy}\right)_x\left(\frac{dv}{dx}\right)_y - p\,\frac{d^2v}{dy\,.\,dx}$$

$$= \left(\frac{dT}{dx}\right)_y\left(\frac{d\varphi}{dy}\right)_x + T\,\frac{d_2\varphi}{dx\,.\,dy} - \left(\frac{dp}{dx}\right)_y\left(\frac{dv}{dy}\right)_x - p\,\frac{d^2v}{dx\,.\,dy}$$

Cancelling equal terms from the two sides

$$\left(\frac{dT}{dy}\right)_x\left(\frac{d\varphi}{dx}\right)_y - \left(\frac{dp}{dy}\right)_x\left(\frac{dv}{dx}\right)_y = \left(\frac{dT}{dx}\right)_y\left(\frac{d\varphi}{dy}\right)_x - \left(\frac{dp}{dx}\right)_y\left(\frac{dv}{dy}\right)_x$$

Leaving out the suffixes and writing in a more simple form, we have

$$\frac{dT}{dy}\cdot\frac{d\varphi}{dx} - \frac{dp}{dy}\cdot\frac{dv}{dx} = \frac{dT}{dx}\cdot\frac{d\varphi}{dy} - \frac{dp}{dx}\cdot\frac{dv}{dy} \quad \dots (2)$$

In this relation, by choosing f or x any y any pair of the four quantities p, v, T, φ, the thermodynamical relations are obtained :—

(1) *Let* $x = \mathrm{T}$ *and* $y = v$, then

$$\frac{d\mathrm{T}}{dx} = 1 \text{ and } \frac{dv}{dy} = 1\ ;\ \frac{d\mathrm{T}}{dy} = 0 \text{ and } \frac{dv}{dx} = 0$$

since T and v are supposed independent. Substituting these values in (2), we get

$$\left(\frac{d\varphi}{dv}\right)_{\mathrm{T}} = \left(\frac{dp}{d\mathrm{T}}\right)_{v}$$

Since $d\varphi = d\mathrm{Q}/\mathrm{T}$,

$$\left(\frac{d\mathrm{Q}}{dv}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{dp}{d\mathrm{T}}\right)_{v} \qquad \dots (3)$$

(2) *Let* $x = \mathrm{T}$ and $y = p$; then

$$\frac{d\mathrm{T}}{dx} = 1 \text{ and } \frac{dp}{dy} = 1\ ;\ \frac{d\mathrm{T}}{dy} = 0 \text{ and } \frac{dp}{dx} = 0.$$

Under these conditions relation (2) becomes

$$\left(\frac{d\varphi}{dp}\right)_{\mathrm{T}} = -\left(\frac{dv}{d\mathrm{T}}\right)_{p}$$

or

$$\left(\frac{d\mathrm{Q}}{dp}\right)_{\mathrm{T}} = -\ \mathrm{T}\left(\frac{dv}{d\mathrm{T}}\right)_{p} \qquad \dots (4)$$

(3) *Let* $x = \varphi$ *and* $y = v$; then

$$\frac{d\varphi}{dx} = 1,\quad \frac{dv}{dy} = 1 \text{ and } \frac{d\varphi}{dy} = \ ,\ \frac{dv}{dx} = 0.$$

Substituting these values in relation (2)

$$\left(\frac{d\mathrm{T}}{dv}\right)_{\varphi} = -\left(\frac{dp}{d\varphi}\right)_{v}$$

or

$$\left(\frac{d\mathrm{T}}{dv}\right)_{\varphi} = -\ \mathrm{T}\left(\frac{dp}{d\mathrm{Q}}\right)_{v} \qquad \dots (5)$$

(4) Let $x = \varphi$ *and* $y = p$; then

$$\frac{d\varphi}{dx} = 1,\ \frac{dp}{dy} = 1 \text{ and } \frac{d\varphi}{dy} = 0,\ \frac{dp}{dx} = 0$$

$$\therefore \qquad \left(\frac{d\mathrm{T}}{dp}\right)_{\varphi} = \left(\frac{dv}{d\varphi}\right)_{p}$$

or

$$\left(\frac{d\mathrm{T}}{dp}\right)_{\varphi} = \mathrm{T}\left(\frac{dv}{d\mathrm{Q}}\right)_{p} \qquad \dots (6)$$

(5) *Let* $x = p$ *and* $y = v$; then

$$\frac{dp}{dx} = 1,\ \frac{dv}{dy} = 1 \text{ and } \frac{dp}{dy} = 0,\ \frac{dv}{dx} = 0$$

$$\therefore \left(\frac{dT}{dv}\right)_p \left(\frac{d\varphi}{dp}\right)_v = \left(\frac{dT}{dp}\right)_v \left(\frac{d\varphi}{dv}\right)_p - 1$$

$$\text{or} \quad \left(\frac{dT}{dp}\right)_v \left(\frac{d\varphi}{dv}\right)_p - \left(\frac{dT}{dv}\right)_p \left(\frac{d\varphi}{dp}\right)_v = 1 \qquad \ldots (7)$$

(6) *Let* $x = T$ *and* $y = \varphi$; then

$$\frac{dT}{dx} = 1, \frac{d\varphi}{dy} = 1 \text{ and } \frac{dT}{dy} = 0, \frac{d\varphi}{dx} = 0$$

$$\therefore -\left(\frac{dp}{d\varphi}\right)_T \left(\frac{dv}{dT}\right)_\varphi = 1 - \left(\frac{dp}{dT}\right)_\varphi \left(\frac{dv}{d\varphi}\right)_T$$

$$\text{or} \quad \left(\frac{p}{dT}\right)_\varphi \left(\frac{dv}{d\varphi}\right)_T - \left(\frac{dp}{d\varphi}\right)_1 \left(\frac{dv}{dT_\varphi}\right) = 1 \qquad \ldots (8)$$

Out of these six thermodynamic relations the one suited for a particular problem is used and the problem solved. Let us give some examples.

(*i*) **Specific heat equation.**

$$C_p = \left(\frac{dQ}{dT}\right)_p = T\left(\frac{d\varphi}{dT}\right)_p$$

$$= T\left(\frac{d\varphi}{dT}\right)_v + T\left(\frac{d\varphi}{dv}\right)_T \left(\frac{dv}{dT}\right)_p$$

Now, $T\left(\frac{d\varphi}{dT}\right)_v = C_v$, and

$$\left(\frac{d\varphi}{dv}\right)_T = \left(\frac{dp}{dT}\right)_v \text{ [Cf. relation (3)]}$$

$$\therefore \quad C_p = C_v + T\left(\frac{dp}{dT}\right)_v \left(\frac{dv}{dT}\right)_p$$

$$\text{or} \quad C_p - C_v = T\left(\frac{dp}{dT}\right)_v \left(\frac{dv}{dT}\right)_p \qquad \ldots\ldots\ldots (1)$$

Taking the general thermodynamic relation $p = f(v, T)$ and differentiating it, we get

$$dp = \left(\frac{dp}{dv}\right)_T dv + \left(\frac{dp}{dT}\right)_v dT$$

For an isobaric process $dp = 0$. Hence the above relation yields

$$\left(\frac{dp}{dT}\right)_v = -\left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p$$

Substituting this value of $\left(\frac{dp}{dT}\right)_v$ in relation (1) we get

$$C_p - C_v = -T\left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p^2$$

Now, the bulk modulus of elasticity E is given by $E = -v\left(\frac{dp}{dv}\right)_T$

and the coefficient of volume expansion α by $\alpha = \frac{1}{v}\left(\frac{dv}{dT}\right)_p$

$$\therefore \quad C_p - C_v = TE\alpha^2 v \qquad \dots (2)$$

(*ii*) **Latent heat equation.** The relation (3), *viz.*,

$$\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v$$

indicates that the isothermal variation of the quantity of heat with volume is equal to the product of the absolute temperature and the variation of pressure with temperature at constant volume. Since the heat supplied at constant temperature changes the volume, the heat absorbed is the latent heat, used in the change of state of the substance. If L is the quantity of heat necessary to change unit mass of the substance from one state to the other, and v_1 and v_2 the corresponding specific volumes of the substance, then

$$\left(\frac{dQ}{dv}\right)_T = \frac{L}{v_2 - v_1},$$

so that

$$\frac{L}{v_2 - v_1} = T\frac{dp}{dT}$$

or

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$$

which is the *Clausius-Clapeyron's latent heat equation*, already derived and discussed.

(*iii*) **Effect of pressure on substances that expand or contract on heating.** Relation (4) *viz.*,

$$\left(\frac{dQ}{dp}\right)_T = -T\left(\frac{dv}{dT}\right)_p$$

can be rewritten as

$$\left(\frac{dQ}{dp}\right)_T = -T\alpha,$$

where α is the coefficient of increase of volume at constant pressure. If α is positive, the substance expands on heating. In such a case $\left(\frac{dQ}{dp}\right)_T$ is negative. When such a substance is compressed, *i.e.*, when dp is $+ve$, the temperature will remain constant only if dQ is negative, *i.e.*, if heat is taken away from the substance. In other words, heat is generated when a substance which expands on heating is compressed. On the other hand, a colling effect will be produced, when a substance which contracts on heating is compressed. These results have been verified by Joule in the case of water below and above 4°C. Thus the thermodynamical theory explains the remarkable fact that water below 4°C cools by adiabatic compression in spite of its internal energy increasing.

(*iv*) **Variation of intrinsic energy with volume.** Taking relation (3),

$$\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v,$$

substituting for $dQ = dU + pdv$, we get

$$\frac{1}{T}\left(\frac{dU + pdv}{dv}\right)_T = \left(\frac{dp}{dT}\right)_v$$

$$\text{or} \quad \frac{1}{T}\left(\frac{dU}{dv} + p\right)_T = \left(\frac{dp}{dT}\right)_v$$

$$\therefore \quad \left(\frac{dU}{dv}\right)_T = T\left(\frac{dp}{dT}\right)_v - p$$

This relation can be used to study the variation of intrinsic energy with volume under isothermal conditions :—

(*a*) In the case of *a perfect gas*,

$$pv = RT \text{ ; hence } \frac{dp}{dT} = \frac{R}{v}$$

$$\therefore \quad \left(\frac{dU}{dv}\right)_T = \frac{RT}{v} - \frac{RT}{v} = 0$$

This means that during an isothermal expansion or compression there is no change in the intrinsic energy. Since there is no rise in temperature, there is no variation in kinetic energy as well. This shows also that there is no inter-molecular attraction in perfect gases.

(*b*) For a *gas obeying Van der Waals' equation*,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

$$p = \frac{R}{v - b} - \frac{a}{v^2}$$

$$\left(\frac{dp}{dT}\right)_T = \frac{RT}{v - b}$$

$$\therefore \quad \left(\frac{dU}{dv}\right)_T = \frac{RT}{v - b} - \frac{RT}{v - b} + \frac{a}{v^2} = \frac{a}{v^2}$$

This relation indicates that as the volume of an actual gas increases the change in the internal energy diminishes. When the volume increases the molecules will go farther apart against inter-molecular attraction, hence work will be done with an increase of potential energy, *i.e.*, of the internal energy. This proves the existence of inter-molecular attraction in actual gases.

The variation of internal energy is very small though finite. When the specific volume is small dU/dv will become large, *i.e.*, under high pressures dU/dv is great, but under low pressures it is small. As the temperature or pressure is made very low the actual gases behave like a perfect gas.

(*c*) For *liquids and solids.* By the principle of intermediate variable

$$\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p$$

$$\therefore \quad \left(\frac{dU}{dv}\right)_T = T\left(\frac{dp}{dv}\right)_T \left(\frac{dv}{dT}\right)_p - p$$

$$= T\,K_T\,\alpha - p$$

where K_T is the bulk modulus of elasticity $\left(\frac{dp}{dv}\right)_T$ and α the co-efficient of volume expansion $\left(\frac{dv}{dT}\right)_p$.

$$\text{For mercury } K_T = \frac{1}{3{\cdot}9 \times 10^{-6}} \text{ and } \alpha = 1{\cdot}81 \times 10^{-4}$$

$$\therefore \quad \left(\frac{dU}{dv}\right)_T = \left(273 \times \frac{10^6}{3{\cdot}6} \times 1{\cdot}81 \times 10^{-4}\right) - 1$$

$$= 12670$$

expressing all pressures in atmospheres.

$\therefore$ dU/dv is of the dimensions of pressure. It is called the internal pressure arising from inter-molecular attraction. The above result shows that for ordinary liquids the force of cohesion is very great but when the temperature is increased, the ratio diminishes until it vanishes when the perfect gas stage is reached.

(*v*) **Joule-Kelvin effect.** The necessary condition of the Joule-Kelvin expansion in the porous plug experiment is that $U + pv$

remains constant, while the pressure changes on the two sides of the throttle valve.

$$U + pv = \text{a constant} \qquad \ldots (1)$$

$$\therefore \quad dU + pdv + vdp = 0$$

$$\text{But} \quad dQ = dU + pdv = Td\varphi$$

$$\therefore \quad Td\varphi + vdp = 0$$

Taking T and p as independent variables and partially differentiating,

$$T\left(\frac{d\varphi}{dT}\right)_p dT + T\left(\frac{d\varphi}{dp}\right)_T dp + vdp = 0$$

Using the thermodynamical relation

$$\left(\frac{d\varphi}{dp}\right)_T = -\left(\frac{dv}{dT}\right)_p$$

$$T\left(\frac{d\varphi}{dT}\right)_p dT - T\left(\frac{dv}{dT}\right)_p dp + vdp = 0$$

$$\text{But} \quad T\left(\frac{d\varphi}{dT}\right)_p . dT = T\frac{dQ}{T . dT} \cdot dT = C_p . dT$$

$$\therefore \quad C_p \frac{dT}{dp} = \left\{T\left(\frac{dv}{dT}\right)_p - v\right\} \qquad \ldots (2)$$

The controlling condition is $U + pv = i$, a constant ; hence the change in temperature dT is produced due to a change in pressure dp under constant enthalpy.

$$\therefore \quad \left(\frac{dT}{dp}\right)_i = \frac{1}{C_p}\left\{T\left(\frac{dv}{dT}\right)_p - v\right\} \qquad \ldots (3)$$

The quantity $\left(\frac{dT}{dp}\right)_i$ is called the *differential Joule-Kelvin effect*. For *a perfect gas*

$$\left\{T\left(\frac{dv}{dT}\right)_p - v\right\}$$

can be readily shown to be equal to zero ; taking the general gas equation $pv = RT$ and differentiating it with respect to v and T ; $pdv = RdT$

$$\text{or} \quad \left(\frac{dv}{dT}\right) = \frac{R}{p} \text{ ; hence } T\left(\frac{dv}{dT}\right) = \frac{RT}{p} = v.$$

$\therefore$ Relation (3) reduces to

$$\left(\frac{dT}{dp}\right)_i = 0,$$

which means the *Joule-Kelvin effect vanishes*. It may be noted that the porous plug experiment provides therefore a decisive means of finding whether a gas is perfect or not.

For *a gas obeying Van der Waals' equation* it can be proved that

$$\left(\frac{dT}{dp}\right)_i = \frac{v}{C_p} \cdot \frac{2a\,(v-b)^2 - bv^2RT}{RTv^3 - 2a\,(v-b)^2}$$

$$= \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \text{ approximately.}$$

When $\frac{2a}{RT} > b$ or $\frac{2a}{Rb} > T$ or $T < \frac{2a}{Rb}$, $\frac{dT}{dp}$ is positive, *i.e.*, when dp is negative dT also is negative, which means there is cooling effect in Joule-Kelvin expansion.

When $T > \frac{2a}{Rb}$ there will be a heating effect in Joule-Kelvin expansion. Hence the temperature of inversion T_i, at which the Joule-Kelvin effect changes its sign is given by $T_i = \frac{2a}{Rb}$, as has already been deduced on p. 416.

For a large cooling effect to be produced the difference of pressure on the two sides of the throttle valve $(p_1 - p_2)$ should be large. This is called the *integral Joule-Kelvin effect.* Integrating, therefore, relation (2) as

$$\int_{T_2}^{T_1} C_p \,.\, dT = \int_{p_2}^{p_1} \left[T\left(\frac{dv}{dT}\right)_p - v \right] dp$$

$$\overline{C}_p\,(T_1 - T_2) = \int_{p_2}^{p_1} C_p \,.\, m \,.\, dp$$

$$\text{where } m = \left\{ T\left(\frac{dv}{dT}\right)_p - v \right\} \Big/ \; C_p = \text{ differential}$$

Joule-Kelvin effect.

$$\therefore \qquad (T_1 - T_2) = M = \text{Intergral Joule-Kelvin effect}$$

$$= \int_{p_2}^{p_1} \frac{C_p}{\overline{C}_p}\, m\, dp$$

where C_p is variable, while $\overline{C}_p$ is constant.

To a first approximation $C_p = \overline{C}_p$.

$$\therefore \qquad M = m\,(p_1 - p_2) \qquad \dots (4)$$

Thus the integral Joule-Kelvin effect is proportionately increased by a large difference of pressure.

Inner mechanism of the Joule-Kelvin effect.

Since $$\left(\frac{d\varphi}{dp}\right)_T = -\left(\frac{dv}{dT}\right)_p$$

relation (3) can be expressed as

$$C_p\left(\frac{dT}{dp}\right)_i = -T\left(\frac{d\varphi}{dp}\right)_T - v$$

But $$Td\varphi = dU + pdv$$

$$\therefore \quad C_p\left(\frac{dT}{dp}\right)_i = -\left(\frac{dU}{dp}\right)_T - \left(\frac{pdv}{dp}\right)_T - v$$

$$= -\left(\frac{dU}{dp}\right)_T - \left\{\frac{pdv - vdp}{dp}\right\}_T$$

$$= -\left(\frac{dU}{dp}\right)_T - \left(\frac{d\,(pv)}{dp}\right)_T \qquad \ldots (5)$$

Relation (5) shows that the Joule-Kelvin effect is the resultant of two effects, represented by

$$-\left(\frac{dU}{dp}\right)_T \text{ and } -\left(\frac{d\,(pv)}{dp}\right)_T$$

respectively. The first of these measures the deviation from Joule's law, while the second the deviation from Boyle's law.

Considering the first term, we find that the internal energy of the gas at constant temperature varies with pressure. This can happen only in case there is inter-molecular attraction. (dU/dp) is intrinsically negative, since that portion of the internal energy which is due to inter-molecular attraction always decreases with increase of pressure. Hence due to deviation from Joule's law alone the Joule-Kelvin effect will be a cooling effect. But upon this is superposed the second effect due to deviation from Boyle's law.

Examining, therefore, the second term, in the light of the compressibility (pv vs. p) curves, at low pressures $\frac{d\,(pv)}{dp}$ is negative, so that a cooling effect will be produced, while for high pressure, *i.e.*, after passing the bend in the curve, $\frac{d\,(pv)}{dp}$ is positive, so that a heating effect will be produced. At the bend itself, *i.e.*, at the minimum point of the curve $\frac{d\,(pv)}{dp} = 0$

(*vi*) **Adiabatic changes.** Taking the thermodynamic relation (5), *viz.*,

$$\left(\frac{dT}{dv}\right)_{\varphi} = -T\left(\frac{dp}{dQ}\right)$$

we see that an isentropic variation of temperature with volume is equal to $-$ T × variation of pressure with quantity of heat at constant volume. Since $\left(\frac{dp}{d\mathrm{Q}}\right)$ is always positive, $\left(\frac{d\mathrm{T}}{dv}\right)_\varphi$ is negative, *i.e.*, as the volume increases the temperature decreases, *i.e.*, *during an adiabatic expansion temperature falls.*

Considering the thermodynamic relation (6), *viz.*,

$$\left(\frac{d\mathrm{T}}{dp}\right)_\varphi = \mathrm{T}\left(\frac{dv}{d\mathrm{Q}}\right)_p$$

it is seen that the isentropic variation of temperature with pressure is equal to T × variation of volume with quantity of heat at constant pressure. Since volume always increases with supply of heat at constant pressure $\left(\frac{dv}{d\mathrm{Q}}\right)_p$ is positive. Hence $\left(\frac{d\mathrm{T}}{dp}\right)_\varphi$ is also positive. Under adiabatic conditions, therefore, temperature increases with pressure, *i.e.*, *during an adiabatic compression temperature rises.*

(*vii*) **Stefan-Boltzmann law of radiation.** According to the electromagnetic theory of radiation, when radiation is incident normally on a perfectly reflecting plane surface, it exerts a pressure on the surface equal to the energy density of the radiation. If, however, the incident radiation is diffused, *i.e.*, incident in all directions the pressure is equally distributed along the three axes, so that it is equal to one-third the energy density. Bartoli proved from thermodynamic considerations that radiation should exert a finite pressure, though small. This fact shows that black body radiation behaves like a gas, as it exerts pressure and possesses energy. Hence thermodynamic laws can be applied to black dody radiation just as in the case of a gas.

Let ε denote the energy density of radiation inside a uniform temperature enclosure at absolute temperature T. Let v be the volume and p the pressure of the radiation. Both ε and p are simply functions of T. The total energy U of the radiation is equal to $\varepsilon\, v$.

Applying the thermodynamical relation

$$\left(\frac{d\mathrm{Q}}{dv}\right)_\mathrm{T} = \mathrm{T}\left(\frac{dp}{d\mathrm{T}}\right)_v$$

to the radiation, since $d\mathrm{Q} = d\mathrm{U} + p\,dv$, we have

$$\frac{1}{\mathrm{T}}\left(\frac{d\mathrm{U} + p\,dv}{dv}\right)_\mathrm{T} = \left(\frac{dp}{d\mathrm{T}}\right)_v$$

or
$$\frac{1}{T}\left(\frac{dU}{dv}+p\right)_T=\left(\frac{dp}{dT}\right)_v$$

or
$$\left(\frac{dU}{dv}\right)_T=T\left(\frac{dp}{dT}\right)_v-p$$

Now
$$\frac{dU}{dv}=\varepsilon \text{ and } p=\frac{\varepsilon}{3}$$

$$\therefore \qquad \varepsilon=\frac{T}{3}\frac{d\varepsilon}{dT}-\frac{\varepsilon}{3}$$

or
$$\frac{4\varepsilon}{3}=\frac{T}{3}\frac{d\varepsilon}{dT}$$

$$\therefore \qquad \frac{d\varepsilon}{\varepsilon}=\frac{4dT}{T}$$

Integrating both sides,

$$\log \varepsilon = 4 \log T + \text{constant}$$

$$\therefore \qquad \varepsilon = \sigma T^4,$$

where σ is the total density radiation constant. This is the Stefan-Boltzmann law.

It may be noted that Boltzmann deduced Stefan's law by imagining the radiation to go through a Carnot cycle. In the above method we have applied directly the general thermodynamical laws on the assumption that black body radiation behaves like a gas.

These few examples clearly bring out not only the essential correctness but also the great importance of thermodynamics.

STATISTICAL NATURE OF THE SECOND LAW

The second law of thermodynamics, essentially based on the actually observed irreversible phenomena and the consequent increase of entropy, in spite of its many successes in various branches of science, appears to labour under a serious difficulty from the point of view of ordinary mechanics. For instance, when one tries to explain by ordinary mechanics irreversible phenomena, such as the production of heat by friction or the diffusion of two gases, grave difficulties are encountered. Molecular movements are supposed to be subject to the laws of classical mechanics and thereby to be essentially reversible. If at a given moment the velocities of all the molecules are imagined to be completely reversed, the gas will retrace exactly all its preceding states in turn In this way the kinetic theory of gases seems to have become powerless to explain irreversible phenomena demanded by the second law of thermodynamics.

Struck by this difficulty, Maxwell made several pertinent remarks upon the subject, which actually contained the solution of the problem in embryo. The second law of thermodynamics had been established by "*macroscopic*" observations, *i.e.* observations made upon objects of appreciable size containing a very large number of molecules. The quantities which occur in thermodynamics are only defined by a mean state of all the molecules contained in a given volume. It is in no sense proved that the second law of thermodynamics remains valid for "*microscopic*" phenomena, *i.e.*, phenomena studied on the molecular scale. It is easy to imagine forms of molecular mechanism leading to results in direct conflict with it.

This Maxwell illustrated by a "*demon engine*" described by him as follows : If we conceive a being whose faculties are so sharp that he can follow every molecule in its course, such a being would be able to do what is at present impossible to us. We have seen that the molecules in a vessel full of gas at uniform temperature are moving with velocities by no means uniform though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform (Maxwell's law of distribution of velocities). Now let us suppose that such a vessel is divided into two portions A and B by a division in which there is a small hole and that the "demon", who can see the individual molecules opens and closes this hole, so as to allow only the faster molecules to pass from A to B and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A in contradiction to the second law of thermodynamics. Such a demon can also effect a separation of two gases mutually diffused without expenditure of work again in contradiction to the second law.

Now, whatever results this demon may achieve by purely mechanical means may also be obtained by a sequence of suitable molecular encounters with no external interference at all. The conclusion seems inevitable and in the light of this argument, the second law of thermodynamics cannot be applied to changes in a gas when they are observed in molecular detail. The conclusion is quite legitimate, because the second law does not hold for individual molecules but is a *statistical law* and has no meaning unless we deal with matter in bulk or in macroscopic state, involving a very large number of individuals.

This discussion brings out the true *statistical nature of the second law of thermodynamics* valid only within the limits imposed by the *laws of probability*. It also shows the reason for the certainty in its truth as the most firmly established of all laws in physical science, for the laws of probability show that the chances of its being violated are so very small as to amount to its certainty in practice.

Boltzmann, considering the fact that, in a homogeneous system made up of a large number of individuals the state of equilibrium corresponds to that of maximum entropy on the thermodynamical side and of maximum probability on the dynamical side, was able to link together the entropy and probability of a state by a famous theorem, known as the *Boltzmann's H-theorem*, which is analytically expressed as

$$\varphi = k \log W,$$

where φ is the entropy and W the probability of the state and k a constant. According to this relation, increase of entropy of a system implies a transition from a less probable to a more probable state of the system as already indicated (*Cf.* p. 499). The universe, therefore, tends toward an equilibrium where all the dissymmetries existing today will be flattened out, where all motion will have stopped and where total obscurity and absolute cold will reign. Such will be the end of the world theoretically.

This relation brings out the nature of the connection between the second law of thermodynamics and the kinetic theory of matter, as both being only statistically true, involving the calculus of probabilities, *i.e.*, the second law of thermodynamics, like the findings of kinetic theory, is perfectly valid in the study of macroscopic phenomena, so that the principle of irreversibility, which is inconceivable from the point of view of ordinary mechanics becomes essentially reasonable in statistical mechanics.

From this conclusion it might appear that the statistical laws hold good only for matter in the macroscopic state, and not for matter in the microscopic state. But, strange as it may appear, with the introduction of new theories concerning the microscopic state of matter, such as the *quantum theory of radiation* and *matter waves*, one is now obliged to extend the statistical nature even to the microscopic, individual constituents of matter, so that the fundamental law of Nature, at all stages, *i.e.*, macroscopic and microscopic, seems to be one of probability. Further elucidation of this interesting discovery belongs to the course on Modern Physics. We might, however, conclude the present course on Heat with a reflection that how a law which was primarily developed for the construction of heat engines has become of such fundamental importance. This shows that in scientific researches no clue that is likely to be fruitful can be overlooked.

QUESTIONS

1. What is meant by a reversible change ? Describe Carnot's cycle and prove that efficiency of all reversible engines working between the same two temperatures depends only on the temperature of the hot and cold bodies.
(*Bombay University 1947, 1948, 1949* ; *Punjab University 1953* : *Utkal University 1954*)

2. What do you understand by a reversible process ? Enunciate and prove Carnot's theorem. (*Delhi University 1956*)

3. Describe Carnot's cycle. Calculate the work done in a cycle of operations. Deduce the efficiency of a Carnot's engine working between two temperatures. (*Madras University*)

4. Describe Carnot's cycle and prove Carnot's theorem. What is meant by a reversible change ? State briefly how Carnot's theorem leads to an absolute scale. (*Delhi University 1952, 1954*)

5. State and explain the significance of the second law of thermodynamics. Show that the efficiency of a reversible engine is maximum.
(*Aligarh University 1950* ; *Punjab University 1957*)

6. Show that no engine can be more efficient than the Carnot's reversible engine. Make a comparison of the Carnot's engine with the conditions obtaining in the Otto cycle. (*Madras University*)

7. Describe a Diesel engine and deduce an expression for its efficiency. Can the Carnot's engine be realised in practice ? (*Punjab University 1949*)

8. Describe with diagrams an Otto engine and deduce an expression for its efficiency. (*Allahabad University 1949*)

9. Describe some kind of internal combustion engine and explain fully how heat is thereby converted into work. Describe its uses and applications and dwell upon its advantages over the steam engine.
(*Allahabad University 1927*)

10. Write an essay on 'Heat engines'. (*Dacca University 1929*)

11. How did Kelvin arrive at the absolute scale of temperature ? Show that the ideal gas scale and the absolute scale are identical. How is the absolute scale realised in practice. (*Delhi University 1956, 1953, 1951*)

12. Explain what you understand by a thermodynamic scale of temperature. Show that it agrees with an ideal gas scale.
(*Bombay University 1953* ; *Punjab University 1953, 1954, 1956, 1957*)

13. Enunciate the second law of thermodynamics. Deduce from this the thermodynamical scale of temperature and discuss how this scale is related to the perfect gas scale. (*Madras University*)

14. In what sense can the second law of thermodynamics be regarded as furnishing an absolute scale of temperature ? How can readings of gas thermometers be reduced to this particular scale ?
(*Allahabad University B.Sc. Hons. 1931*)

15. Define a scale of temperature without making use of the peculiarities of any selected thermometric substance. Show (*a*) that Kelvin's work scale is such a scale, and (*b*) that the ratio of two temperatures as measured on the Kelvin scale is identical with the ratio of the same two temperatures on the perfect gas scale. (*London B.Sc.*)

16. What is meant by (*a*) the thermodynamic scale of temperature, (*b*) the perfect gas scale of temperature. (*c*) the platinum resistance scale of temperature. What are the advantages and disadvantages of each ? (*Cambridge*)

17. Derive Clapeyron's equation

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}.$$

Calculate the change in temperature of the boiling point of water due to a change of pressure of 1 cm. of mercury (L = 536 calories, volume of 1 gm. of water at 100°C = 1 c.c., volume of 1 gm. of saturated steam at 100°C = 1600 c.cs. [**Ans.** 0·36°C.] (*Delhi University 1955*)

18. Give an elementary proof of Clapeyron's equation

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}.$$

Discuss how the boiling point of a liquid and the melting point of a solid are affected by change of pressure. (*Punjab University 1949, 1957*)

19. Find an expression for the change in the melting point of a substance with the pressure upon it, stating precisely the units employed in expressing each of the quantities involved. Contrast the effects on two classes of substances, illustrating your answer by examples. (*London B.Sc.*)

20. Show from thermodynamical principles how the relative position on a *p-v* diagram of isothermals for a substance in the solid and liquid states together depends on whether the melting of the solid is accompanied by expansion or contraction.

Indicate on the *p-v* diagram the shape of isothermals of substances of the two classes. (*Tripos Part I*)

21. Deduce the latent heat equation

$$d\theta = \frac{\theta(v_2 - v_1)}{L}\, dp.$$

Calculate the depression of the melting point of ice per atmospheric increase of pressure, given latent heat of fusion = 80 cals., and

$$\frac{\text{density of ice at } 0°\text{C}}{\text{density of water at } 0°\text{C}} = \frac{10}{11}.$$ [**Ans.** 0·0081°C]

(*Nagpur University 1930*)

22. Prove that

$$\frac{dp}{d\theta} = \frac{L}{\theta\,(v_1 - v)}.$$

One gram of water vapour at 100°C and atmospheric pressure occupies a volume of 1640 c.cs. and L = 536 calories. Prove that the vapour pressure of water at 99°C is about 733 mm. of mercury. (*Allahabad University M.Sc. 1926*)

23. Establish the relation

$$\frac{dL}{dT} - \frac{L}{T} = s_2 - s_1.$$

Calculate the specific heat of saturated steam at 100°C given the following data L at 90°C = 545·25 cals., L at 100°C = 539·3 cals., L at 110°C = 533·17 cals., and specific heat of water at 100°C = 1·013. [**Ans.** −1·036]

(*Madras University*)

24. Calculate the volume of a gram of steam at 100°C, given that the latent heat of evaporation of water at 100°C = 535 and the change of boiling point is 0·37°C per cm. of mercury pressure, ($J = 4{\cdot}2 \times 10^7$). [**Ans.** 1674 c.cs.]

(*Manchester B.Sc.*)

25. Discuss the effect of change of pressure on the boiling point of a liquid.

Assuming that the specific volumes of water and saturated steam at 100°C are 1 c.c. and 1601 c.cs. respectively and the latent heat of vaporisation is 536 cals./gm., find the change in the boiling point for a change of pressure of 1 cm. of mercury. [**Ans.** 0·362°C.]

(*Allahabad University 1946 ; Calcutta University 1948*)

26. Calculate the latent heat of ice given that change of pressure of one atmosphere changes the melting point of ice by 0·0074°C and when one gram of ice melts volume changes by 0·0907 c.c. [**Ans.** 80·8 calories.]

(*Punjab University 1957*)

27. Prove the latent heat equation

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1.$$

Calculate the specific heat of saturated steam from the above equation and explain the meaning of its negative value. Given L = 539·3 cals., T = 100°C, $\frac{dL}{dT} = -0{\cdot}640$, $C_1 = 1{\cdot}01$. [**Ans.** −1·075.]

(*Allahabad University 1955 ; Baroda University 1953 ;
Nagpur University 1956*)

28. Explain the terms : *entropy* and *isentropics*. Show that the entropy of a system tends to a maximum. Represent the Carnot cycle on a temperature-entropy diagram and prove that its area represents available energy. Establish directly from the above that the efficiency of an engine is $(T_1 - T_2)/T_1$ where T_1 and T_2 are the temperatures between which the engine works.

(*Madras University*)

29. Explain what you mean by the entropy of a substance. Show that for any reversible cyclic change of a system the total change of entropy is zero. Explain why this statement is not true for irreversible changes.

(*Baroda University 1955 ; Punjab University 1958*)

30. Explain the idea of entropy. Derive an expression for the entropy of *m* gms. of perfect gas.

(*Allahabad University 1950*)

31. A volume of a gas expands isothermally to four times its initial volume. Calculate the change in its entropy in terms of the gas constant.
[**Ans.** 1·3854 R]. (*Baroda University 1954*)

32. What do you understand by the statement "the entropy of a system tends to a maximum". What change of entropy occurs when 50 gms. of steam at 100°C are converted to water at the same temperature. L of steam = 536 cals. [**Ans.** 71·86 cals./°C] (*Madras University*)

33. What do you understand by entropy ? State the second law of thermodynamics in terms of entropy.

Calculate the change in entropy when m gms. of a liquid of specific heat s are heated from $T_1°$ to $T_2°$ and then converted into its vapour without raising its temperature. (Latent heat at $T_2° = L$) (*Allahabad University 1941*)

34. Define entropy. What is its physical significance ? Show that the entropy remains constant in a reversible process but increases in an irreversible one. (*Allahabad University, 1936*)

35. Prove the thermodynamical relation

$$\left(\frac{dQ}{dv}\right)_T = T\left(\frac{dp}{dt}\right)_v$$

Calculate under what pressure ice would freeze at −1°C, change of specific volume when 1 gm. of water freezes into ice being 0·091 c.c. Given $J = 4{\cdot}2 \times 10^7$, one atmosphere $= 10^6$ dynes/cms.^{2} and latent heat of fusion of ice = 80 calories. [**Ans.** 135·2 atmospheres] (*Allahabad University, 1956*)

36. Prove the thermodynamical relation.

$$\left(\frac{d\varphi}{dv}\right)_\theta = \left(\frac{dp}{d\theta}\right)_v$$

and hence prove

$$L = \theta\,\frac{dp}{d\theta}\,(v_2 - v_1).$$

(*Benares Hindu University, 1951*)

37. Prove the thermodynamical formula

$$\left(\frac{dQ}{dp}\right)_T = -\,T\left(\frac{dv}{dT}\right)_p$$

Hence show that heat is generated when a substance which expands on heating is compressed and for substances which contract a cooling should take place. (*Roorkee University, 1953*)

38. Define entropy. Prove from the principles of thermodynamics that the decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase of volume per unit increase of temperature under constant pressure. Hence show that heat is generated when a substance, which expands on heating, is compressed.

(*Allahabad University, 1938*)

39. The destiny of the physical universe is stagnation. Discuss this statement.

40. Give an account of any violations of the second law of thermodynamics which have been suggested and discuss fully the light which they throw on the real nature of that law.

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